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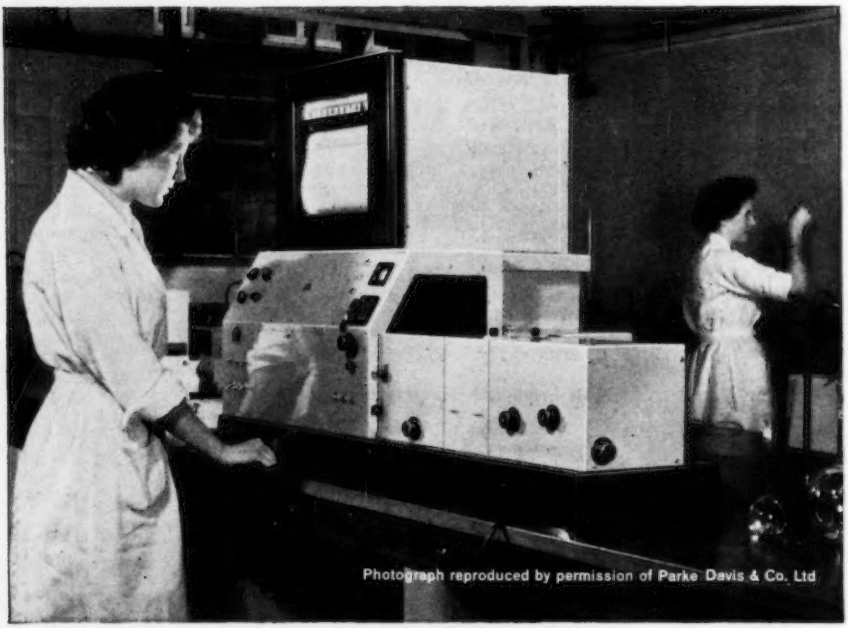

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

4441. **Analytical reviews, 1961. Applications.** *Anal. Chem.*, 1961, **33** (5).—The following contributions are included. **Air pollution,** J. P. Lodge, jun., 3R–13R. **Clinical chemistry,** G. R. Kingsley, 13R–32R. **Coatings,** M. H. Swann, M. L. Adams and G. G. Esposito, 33R–37R. **Essential oils and related products,** E. Guenther, K. Kulka and J. A. Rogers, 37R–45R. **Fertilisers,** E. D. Schall, 46R–49R. **Food,** J. C. Cavagnol, 50R–61R. **Solid and gaseous fuels,** W. H. Ode and T. Christos, 61R–69R. **Ferrous metallurgy,** H. F. Beeghly and L. C. Pasztor, 70R–75R. **Non-ferrous metallurgy,** C. J. Leftault, jun., and M. L. Moss, 76R–87R. **Pesticides,** W. E. Westlake, 88R–91R. **Petroleum,** R. L. LeTourneau, 92R–112R. **Pharmaceuticals and related drugs,** G. J. Papariello, S. C. Slack and W. J. Mader, 113R–126R. **Natural and synthetic rubbers,** F. J. Linnig, M. Tryon and E. J. Parks, 127R–137R. **Water analysis,** M. W. Skougstad and M. J. Fishman, 138R–164R.

4442. **The repercussions of nuclear developments on analytical chemistry.** G. Duyckaerts (Univ. de Liége, Belgium). *Chim. Anal.*, 1961, **43** (4), 178–188.—A review is presented of modern trends in analytical nuclear science, with special reference to radioactive tracers, isotopic dilution methods in elementary and molecular analysis, activation analysis and radiometric analysis. New phosphorus compounds for analysis by extraction, and the separation of transplutonium elements, are also discussed. (22 references.) R. A. HENDEY

4443. **Rationalisation of the expression of analytical results. Molecular index or equivalent weights.** S. Veibel (Lab. de Chim. Org., Tech. Univ., Copenhagen, Denmark). *Chim. Anal.*, 1961, **43** (4), 189–190.—The method of expression of analytical results in the form of "molecular indices" instead of the conventional analytical values, *e.g.*, acetyl value and hydroxyl value, is further discussed, with examples (*cf.* Hennart and Merlin, *Ibid.*, 1960, **42**, 490). It is suggested that a reasonable idea of the structural formulae can be deduced from the figures obtained. R. A. HENDEY

4444. **Use of hydrazine to accelerate the rate of hydrogen sulphide evolution from thioacetamide solutions.** D. M. King and F. C. Anson (California Inst. of Technol., Pasadena, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 572–575.—The liberation of H_2S from thioacetamide soln. is a first-order reaction with respect to both thioacetamide and hydrazine. Rate constants have been determined at pH 4·5 to 6·0. Working at 50° and pH 5·5, and with approx. molar concn. of reagents in the final soln., readily collected ppt. of metal sulphides are obtained.
T. R. ANDREW

4445. **Ethyldithiocarbamate as a substitute for hydrogen sulphide.** Binayendra Nath Sen (Syamsundar College, Syamsundar, West Bengal, India). *Anal. Chim. Acta*, 1961, **24** (4), 386–387 (in English).—The reagent is prepared by gradual addition of CS_2 to ethylamine [33% (w/v)] with cooling. Excess of CS_2 is removed on a water bath. The ppt. formed with Hg^{+}, Pb^{2+}, Hg^{2+}, Bi^{3+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} are described. All the ppt. were either sulphides or hydrated sulphides which changed to sulphides on warming or standing. The reagent is fairly stable.
A. J. BENNETT

4446. **Analytical use of dithiocarbamates.** V. N. Podchaĭnova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 146–164; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D17.—The dithiocarbamates described in the literature, and their use in analytical chemistry, are briefly reviewed. It is shown by optical and potentiometric methods that diethyldithiocarbamate forms with Cu a compound with the components in the ratio 2:1. Various methods (photometric surface treatment, photometric, colorimetric) are developed for the determination of Cu in steel, metallic nickel, cadmium, and manganese ores, based on measurement of the intensity of colour of the extract of Cu dithiocarbamate in CCl_4. Interfering ions are masked with $Na_4P_2O_7$ and EDTA (disodium salt) in ammoniacal medium. One determination takes 30 to 35 min. (83 references.)
C. D. KOPKIN

4447. **Analytical properties of hydroxyquinones. I. Derivatives of 2,5-dihydroxy-*p*-benzoquinone.** I. S. Mustafin, L. O. Matveev and E. A. Kashkovskaya. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 87–96; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D16.—The sensitivities of the reactions of dihydroxy-*p*-benzoquinone derivatives (2,5-dihydroxy-*p*-benzoquinone, chloranilic, bromanilic, iodanilic and nitranilic acids) with the alkaline-earth metals are determined. The "weight effect" is not always observed in the halo-anilic acid series or in the reaction of one derivative with various cations. It is shown conductimetrically that the halo-anilic acids are similar in strength of reaction. The absorption of the acids themselves and of their Na salts is studied, and the influence of concn. on the mol. extinction coeff. of the halo-anilic acids is established; this is explained by internal hydrogen bonding.
C. D. KOPKIN

4448. **8-Mercaptoquinoline (thio-oxine) as an analytical reagent.** Yu. A. Bankovskiĭ, A. F. Ievin'sh and V. I. Kuznetsov. Symposium: "Khimiya, Tekhnologiya i Primenenie Proizvodnykh Piridina i Khinolina," Akad. Nauk LatvSSR, Riga, 1960, 271–281; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D18.—8-Mercaptoquinoline reacts with cations that give sulphides stable in aq. soln. to form internally complexed compounds of intense colour and good solubility in org. solvents.

Selective and sensitive methods are developed for the determination of Cu, Mo, Pd, Re, Hg, Au and Ag, the mercaptoquinoline complexes of which are formed in fairly acid soln. 8-Mercaptohaloquinolines, which are more stable to atmospheric oxidation, are also studied as reagents. The solubility of the resulting complexes in org. solvents depends on the position of the substituent, being greater with the halogen in the 3- or 5-position (which increases the acidic properties of the –SH group) and less with 6-substitution (which decreases the basic properties of the N). C. D. KOPKIN

4449. **Dialkyl and diaryl phosphorodithioates as analytical reagents. VIII. Reaction of dialkyl and diaryl phosphorodithioic acids with ions.** A. I. Busev and M. I. Ivanyutin. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 172–191; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D19.—The reactions of dialkyl and diaryl phosphorodithioic acids with ions of a large number of elements are described. The properties and possible applications in analytical chemistry (for gravimetric, titrimetric and photometric determinations) of their compounds with Cu, Ag, Cd, Hg^{2+}, In, Tl^{+}, Sn^{2+}, Pb, As, Sb, Bi, Mo^{5+}, Se^{4+}, Te^{4+}, Fe, Ni, Co, Ru, Rh, Pd, Pt, Os and Ir are indicated. The solubility series of the diethyl phosphorodithioates is established, and coincides in the main with the solubility series of the sulphides and xanthates. *Cf. Anal. Abstr.*, 1959, **6**, 1634, 2527.)
C. D. KOPKIN

4450. **The adsorption of coloured products from colour reactions.** L. Rosenthaler (Seftigenstrasse 40, Berne, Switzerland). *Z. anal. Chem.*, 1961, **180** (3), 171–174 (in German).—If a few drops of 10% $MgSO_4$ soln. are added to an alkaline soln. in which a colour reaction has occurred the coloured product is often adsorbed on the pptd. $Mg(OH)_2$. This effect, used by Pittarelli (*Bull. Acad. Méd.*, 1920, **84**, 132) for the detection of acetaldehyde by the formazan reaction, has now been applied to 9 colour reactions for a number of compounds. Colours of the soln. and the ppt. are tabulated. In favourable cases, owing to the concentrating effect of the adsorption, a concn. of 1 in 10^7 may be detected, even when the soln. itself is not visibly coloured. The ppt. may be coated with a colourless lacquer and preserved for demonstration.
G. RUSSELL

4451. **Some corrections necessary for the achievement of the highest accuracy in micro-analytical weighing.** W. Dürselen (Inst. Microbiol. and Exp. Therapy, German Acad of Sci., Jena). *Z. Chem.*, 1961, **1** (4), 119–123.—The accuracy with which several corrections must be made, so that the mean error of a single weighing is $< \pm 2$ μg, is considered. For the correction due to buoyancy of the object and the weights, a direct determination of air density by weighing a quartz globe, evacuated and then full of air, is recommended. The buoyancy error due to tilt of the beam is also considered and the correction makes use of the pointer scale value (mg per scale division, incorrectly called sensitivity). It is advisable to keep the tilt of the beam, *e.g.*, in aperiodic balances, within a small range. The mass of a small object is proportional to the tangent of the angle of the beam, whereas the pointer describes an arc. Equations for deriving the necessary corrections are given.
G. RUSSELL

4452. **Radiometric precipitation in filter-paper: a rapid method of micro-analysis.** M. Thackray (Australian Atomic Energy Comm., Res. Estab., Lucas Heights, N.S.W.). *Nature*, 1961, **190**, 434–435.—Apply the sample soln. to a disc of filter-paper, evaporate to dryness and immerse in a soln. of a radioactive reagent to form a ppt. in the pores of the paper. Remove the unpptd. radioactive materials by washing, dry the disc and compare the count with that of discs prepared similarly from standard soln. The method has been used for the determination of microgram quantities of Be as $BeNH_4{}^{32}PO_4$, Mg as $MgNH_4{}^{32}PO_4$, and Cl^- (> 30 μg) as $^{110m}AgCl$. A. R. ROGERS

4453. **Redox indicators in non-aqueous cerimetry.** G. Prabhakar Rao and A. R. Vasudeva Murthy (Dept. Inorg. Phys. Chem., Indian Inst. Sci., Bangalore, India). *Z. anal. Chem.*, 1961, **180** (3), 169–171 (in English).—Some redox indicators used in aq. soln. are satisfactory for the titration of quinol (**I**) in glacial acetic acid. *Procedure*—Pipette an aliquot (2 to 5 ml) of 0·05N-**I** in acetic acid into a 25-ml conical flask, and add acetic acid (10 ml) and 2 drops of indicator soln. in acetic acid. Titrate with 0·05N-$(NH_4)_2[Ce(NO_3)_6]$ in methyl cyanide. Sharp colour changes ($\simeq$0·03 ml) were given by ferroin (0·025M), diphenylamine (0·25%), methyl red (0·1%) and Janus Green (0·1%). The last two indicators did not give reversible colour changes. Phenosafranine and neutral red were unsatisfactory. In 8 experiments (2 with each satisfactory indicator) a mean error of $\pm$0·4% was obtained. G. RUSSELL

4454. **Fast Navy 2R as indicator for EDTA titrations and its application for determination of mercury in some pharmaceutical preparations.** A. A. Abd El Raheem and M. M. Dokhana (Drug Anal. Admin., Agouza, Cairo, U.A.R). *Z. anal. Chem.*, 1961, **180** (5), 339–348 (in English).—Solochrome Fast Navy 2R (C.I. Mordant Blue 9) is a satisfactory indicator for the titration at pH 8·5 of Ca, Mg, Ni, Zn, Cd, Mn or Pb with EDTA. Mercury does not give any colour with this reagent so that Hg compounds may be determined after destruction of organic matter with $HClO_4$ - HNO_3, by addition of an excess of EDTA and back-titration with 0·01M-$ZnSO_4$. The agreement between results by this method and by the B.P.C. (1954) method for Hg is usually within 1·5%. T. R. ANDREW

4455. **The use of some nitroarylalkanes as indicators for non-aqueous titrations.** I. M. Korenman, E. M. Perepletchikova and V. S. Étlis. *Trudy Khim. i Khim. Tekhnol.* [*Gorkiĭ*], 1960, **2**, 284–287; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D159.—For the determination of organic acids by titration with alkali in non-aqueous media the indicator proposed is di-(2,4-dinitrophenyl)methane, used as a 1% soln. in dioxan. A. BURWOOD-SMITH

4456. **Use of iodine chloride for the amperometric titration of sodium sulphite, stannous chloride, Rivanol [ethacridine lactate] and quinine hydrochloride.** A. I. Gengrinovich, L. E. Korneva and A. M. Murtazaev. *Trudy Tashkent. Farmatsevt. Inst.*, 1960, **2**, 355–358; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D29.—A method is developed for the titration of these compounds with ICl soln. at a rotating platinum electrode without an external e.m.f. from the current due to I^+. The titration of Na_2SO_3 and $SnCl_2$ is based on their oxidation by the ICl soln., of ethacridine lactate on a substitution

reaction to form a mono-iodo product, and of quinine hydrochloride on the addition of ICl to the vinyl group of the quinine. Place the test soln. in a titration vessel, dilute to 40 ml and titrate with a 0·1N-HCl soln. of ICl ($SnCl_2$ is titrated in the presence of $CaCO_3$). The reaction with Na_2SO_3, $SnCl_2$ and ethacridine lactate is complete in 2 to 3 min., and with quinine hydrochloride in 20 to 25 min. Small amounts of these substances can be reliably determined with good reproducibility.

C. D. KOPKIN

See also Abstracts—**4464**, Quercetin as colour reagent. **4481**, Sodium in potassium dichromate. **4483**, **4644**, **4660**, 1,2-Di-(*o*-aminobenzylideneamino)-ethane as reagent for Cu and Ni. **4521**, *NN'*-Ethylenedianthranilic acid as reagent for Al. **4608**, Trihydroxyfluorone derivatives as reagents for Te. **4887**, *NN*-Diformyl-2-methylpiperazine as stationary phase in gas chromatography.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

4457. **Reactor technology report No. 14. Chemistry.** *U.S. Atomic Energy Comm.*, Rep. KAPL-2000-11, 1960. 115 pp.—The following papers of analytical interest are included. **Analysis of tantalum and lutetium in irradiated hafnium,** R. F. Dufour. **Voltammetry with a mercury-pool cathode,** D. P. Stricos. **Polarographic determination of niobium in zirconium-base alloys,** D. P. Stricos. **Determination of lead and tellurium in lead-tellurium alloys,** O. J. Articolo. **Separation of micro amounts of hafnium from macro amounts of zirconium by cation exchange,** F. W. Walker.

METALLURG. ABSTR.

4458. **Separation of metallic elements by anion-exchange resins. I. Study of the fixation of some complex chlorides.** B. Trémillon (École de Phys. et de Chim., 10 rue Vauquelin, Paris, France). *Bull. Soc. Chim. France*, 1961, (2), 275–281.—The various equilibria that obtain when soln. of chlorides of elements such as Zn, Cd and Hg are in the presence of an anion exchanger are considered, and it is shown theoretically that fixation should be a max. when the concn. of the neutral undissociated salt MCl_2 is a max., and this is shown experimentally to be so. The determination of the partition of the element between resin and soln. in various concn. of NaCl soln. shows that the concn. of Cd reaches a max. on the column with 1 mole saturating 2 equiv. of exchange capacity, and this is interpreted as meaning that the Cd is fixed largely as $CdCl_4^{2-}$; Zn does not reach this limit and this is interpreted as a less energetic fixation as $ZnCl_4^{2-}$ and $ZnCl_3^-$. The results allow equilibrium constants to be determined. Mercury is fixed more energetically and does not reach a limit, and the fixation exceeds the max. theoretical capacity of the resin. This is interpreted as being due to the high concn. of $HgCl_2$ in soln. not only causing an increase in $HgCl_4^{2-}$ on the resin, but also leading to considerable adsorption and fixation as $HgCl_2$. The effect of acetone, which stabilises the species MCl_2, on the soln. is studied and it is shown to increase the fixation according to expectation.

II. Frontal analysis and displacement development of zinc and cadmium chlorides. B. Trémillon. *Ibid.*, 1961, (2), 281–286.—The curves of partition concn. in various concn. of NaCl, of $ZnCl_2$ and $CdCl_2$ on Dowex-2 resin, can be considered as analogous to the adsorption isotherms of adsorption chromatography. The conditions for frontal analysis and displacement development are discussed and applied to the separation of $ZnCl_2$ and $CdCl_2$.

E. J. H. BIRCH

4459. **Separation of elements by complex-formation chromatography.** I. D. Muzÿka and V. A. Molodtsova. *Ukr. Khim. Zhur.*, 1960, **26** (4), 535–539; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D47.—A method is developed for the purification of $ZnSO_4$ soln. from Fe^{3+}, Cu^{2+} and Ni^{2+} based on adsorption of the impurities on a column containing layers of pure carbon and its mixtures with dimethylglyoxime (**I**) and ZnO. The soln. is filtered, with suction, through the column (diam. 8 mm, height 25 cm) at a rate of 100 ml per sq. cm per hr. A column containing a mixed adsorbent of carbon and 10% of **I** adsorbs 25·5, 2·4, 1·7 and 15·6 mg of Cu, Fe, Co and Ni, respectively, per g of carbon. With an increased **I** content, the adsorption of Cu and Ni increases, that of Co is almost unchanged, and that of Fe remains the same. The adsorption of Fe on a column containing carbon and ZnO increases linearly with increase of the ZnO content; Ni is adsorbed to the same extent as on pure carbon. On a column (165 cm × 14 mm) containing 4 g of BAU carbon (grain size 0·75 mm) as a lower layer and 4 g of a mixed adsorbent (4 g of carbon, 0·5 g of **I** and 0·1 g of ZnO) as an upper layer, and with a rate of filtration of 68 ml per sq. cm per hr., 1860 ml of a $ZnSO_4$ soln. containing Zn 100 g per litre and Fe 2·5, Cu 5·0, Co 5·0, and Ni 7·1 mg per litre was purified to impurity contents of Fe 0·77, Cu < 0·06, Co 0·4, and Ni 0·1 mg per litre. An even more effective separation was attained on a similar column containing 5 g of carbon OU as lower layer and a mixture of 10 g of carbon, 3 g of **I** and 0·5 g of ZnO as upper layer; the column also contained 50·3 mg of Na diethyldithiocarbamate. The pH of the initial soln. was 3·9, and that of the filtrate 4·5. Nickel and Cu could not be detected chemically in the filtrate, and the Fe content was 0·2 mg per litre.

C. D. KOPKIN

4460. **Titrimetric determination of small amounts of elements with dyestuffs.** V. P. Zhivopistsev. *Trudÿ Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 52–57; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D76.—In acid medium in the presence of SCN^-, tetramethyldiaminodiphenylantipyrinylmethanol (**I**) and dibenzyldimethyldiaminodiphenylantipyrinylmethanol form poorly sol. compounds with Zn, Co, Hg, Mo, Bi and Cd. A titrimetric method has been developed for the determination of Zn with **I**. To 20 ml of soln. (< 0·01 g of Zn) containing 7 to 8% of NH_4SCN and 0·5N to 1N in HCl, add 2 to 3 ml of light petroleum and titrate with 0·01N to 0·02N-**I** in N-HCl. The resulting blue ppt. collects at the surface of the soln. The appearance of the red colour of **I** indicates the end-point. In the presence of Fe (< 1%) or Cu, after acidifying the soln. add a few drops of 10% NH_4SCN soln., heat to 60° to 70° and add dropwise 10% ascorbic acid soln. till the soln. is decolorised, and 1 to 2 ml in excess. Cool, filter off the ppt., wash it with N-HCl, and determine Zn in the filtrate with **I** soln. as described above. The relative error in the determination of Zn is 3%. There is no

interference from Al, Mn, Mg, the alkali and alkaline-earth metals, $<2\%$ of Cr or $<10\%$ of Ni. Poorly sol. compounds are formed between **I** and Co, Cu, Bi, Mo, Sn, W, Cd and Fe, and these interfere in the determination of Zn. To prepare **I**, mix 25 g of Michler's ketone (**II**) and 35 g of phenazone, add 25 ml of $POCl_3$, heat for 3 hr. under reflux on a water bath and then for 3 hr. on an oil bath at 110° to 120°, cool, add 150 to 200 ml of water (heat slightly to accelerate dissolution), cool to 1° to 2° and destroy excess of phenazone by adding cold 20% NaOH soln.; **I** and unchanged **II** are then pptd. Filter off the ppt., wash it with water, dissolve it in a small vol. of 2N-HCl, and precipitate **I** at 1° to 2° with conc. $ZnCl_2$ soln. Filter off the complex of Zn with **I**, wash it with conc. $ZnCl_2$ soln. and treat it with 25% aq. NH_3; Zn dissolves and **I** remains as the residue. For the complete removal of Zn, filter off the residue, wash it with water, dissolve it in 2N-HCl, and filter into 25% aq. NH_3. Again filter off the pptd. **I**, wash it with water, and dry it over H_2SO_4. C. D. KOPKIN

4461. **Spectrochemical determination of trace elements in inorganic salts using a concentration - precipitation technique.** R. L. Dehm, W. G. Dunn and E. R. Loder (Ind. Lab., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 607–609.—Impurities in salts of Na and K are concentrated by pptn. from aq. soln. (10-g sample) at pH 9·0 with 8-hydroxyquinoline and thionalide after addition of 1 mg of Al (1 ml of a 1·1% soln. of $AlCl_3.6H_2O$). The ppt. is filtered off, ashed and examined spectrographically after being mixed with 10 mg of matrix mixture (50 parts of Li_2CO_3, 1 of GeO_2, 40 of graphite and 0·30 of Bi_2O_3). Copper, Zn, Mn, Pb, Sn, Ni and Fe are determined by using Ge and Bi as internal standards. The range of impurity concn. covered is from 0·1 to 5 p.p.m. T. R. ANDREW

4462. **Paper electrophoresis of some metal ions in sulphate solutions.** H. C. Chakrabortty (Lab. Curie, Inst. du Radium, Paris, France). *J. Chromatography*, 1961, **5** (2), 121–125 (in French).—Tervalent aluminium, Cr^{III} and Fe^{III}, in 0·5M-Na_2SO_4 containing enough H_2SO_4 to make the pH 1·0, move very slowly during electrophoresis. In N-H_2SO_4, however, they move much more quickly, and behave as cations. The difference in behaviour is attributed to the formation of ions such as $[M(H_2O)_4SO_4]^+$ and $[M(H_2O)_4(SO_4)_2]^-$ in soln. with a high concn. of SO_4^{2-}. Some other tervalent metals, including Ga, In, Sc, La and Y, and some quadrivalent metals, *e.g.*, V and Ge, behave similarly. Bivalent metals move more rapidly, and monovalent metals move more rapidly still. Useful separations can be obtained of Al^{III}, Fe^{III}, Th^{IV} and UO_2^{2+}; of Cd^{II}, Pb^{II} and Bi^{III}; of Al^{III} and Zr^{IV}; and of Y^{III}, La^{III} and Sc^{III}.
R. M. ROWLEY

4463. **Spectrophotometric determination of metals by extraction with 8-hydroxyquinoline and 8-hydroxy-2-methylquinoline in chloroform.** Kenji Motojima and Hiroshi Hashitani (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Japan Analyst*, 1960, **9** (2), 151–161.—Conditions for the extraction of 18 metals are presented. K. SAITO

4464. **Colour and fluorescence reactions with quercetin.** I. M. Korenman, F. R. Sheyanova and Z. F. Shcherbakova. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1960, (2), 303–306; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D40.—The sensitivities of the fluorescence reactions of quercetin with Be^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Y^{3+}, La^{3+}, Zn^{2+} and Mg^{2+} are determined, and the optimum pH ranges established. The most sensitive reaction is with Be^{2+}, which occurs at pH 1 to 10. Of the anions, only BO_3^{3-} and $B_4O_7^{2-}$ give the fluorescence reaction, at pH 7 to 11. With Tl^{3+} quercetin forms a violet compound, extracted with $CHCl_3$, which is suitable for the detection of Tl. The colour of the extract is stable for 30 min. The optimum pH is 3 to 6, the limiting concn. 1 in 10^5 and the detectable minimum 0·01 μg of Tl per ml; Tl^+ are first oxidised to Tl^{3+} with bromine water, the excess of which is removed by boiling. Under these conditions, other oxidants (MnO_4^-, $Cr_2O_7^{2-}$ and $S_2O_8^{2-}$) give a pale-pink colour only at concn. of 1 mg per ml. By using ^{204}Tl it is shown that $\simeq 50\%$ of the Tl passes into the $CHCl_3$ layer. C. D. KOPKIN

4465. **Analysis of permanent gases by gas - solid chromatography using an ionisation method for detection.** J. F. Ellis and C. W. Forrest (U.K.A.E.A., Development and Engineering Group, Research and Development Branch, Capenhurst, Chester). *Anal. Chim. Acta*, 1961, **24** (4), 329–333 (in English).—The use of He as carrier gas with a Lovelock detector is applied to the analysis of mixtures of H, O, N, CH_4 and CO. The standing ionisation current in the detector is carried by impurities in the He. Helium atoms excited to a metastable state by a radioactive source are able to ionise these impurities. When an excess of an eluted foreign gas appears in the detector many electrons from the radioactive source lose energy by collision with the foreign gas molecules without ionising them. These electrons then have insufficient energy to excite He atoms and the ionising process is cut down. Thus with a detector potential of 1250 V, strong and repeatable negative signals were obtained during elution of H, O, N, CH_4 and CO. Accuracies are comparable with those obtained with the best katharometers without the need for such accurate control of flow or temperature. An ultimate detection level of 0·1 μl of gas at s.t.p. can be obtained. Re-calibration is essential when the helium-supply cylinder is changed. A. J. BENNETT

4466. **Determination of oxygen, hydrogen, nitrogen and carbon in metals. A review.** W. G. Guldner (Bell Telephone Lab. Inc., Murray Hill, N.J., U.S.A.). *Talanta*, 1961, **8** (4), 191–202 (in English).—A review with 22 references.
G. S. ROBERTS

4467. **Spectrographic determination of hydrogen in alloys.** E. S. Kudelya and O. P. Ryabushko. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 183–189; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D86.—The method described is suitable for the determination of H in titanium alloys, chrome-nickel and carbon steels and in welds. Spectra are excited with three successive low-voltage impulse discharges in Ar at a pressure of 2 atm., and the lines H 6562·85 and N 6610·85 A are used. A tungsten rod (diam. 4 to 5 mm) with a conical tip serves as the electrode. Curves are constructed showing the relationship between the entry of H into the spark gap and the number of discharges acting on one and the same portion of sample. It is shown that, in an atmosphere of Ar, the intensity of the H lines for aluminium and titanium alloys and chrome-nickel steel is reduced as the number

of impulses increases. This shows the relatively low mobility of H in these alloys. With Ti-free steel, the intensity of the H line at first increases and then remains practically constant; this shows the establishment of dynamic equilibrium between the discharge of H and the rate of its entry from the interior. It is shown that in an atmosphere of Ar a single discharge destroys only the surface layer of the sample. This permits of a local, layer-by-layer determination of H. The method can be used to determine more than 0·008% of H in titanium alloys and more than 0·0002% of H in steel with a mean error of ±6% and ±10%, respectively. Satisfactory agreement is obtained between these results and those obtained by heating the sample *in vacuo*. K. R. Cook

4468. **Methods and results of the spectrographic determination of gases in metals.** S. A. Skotinkov. *Trudy Inst. Metallurg., Akad. Nauk SSSR*, 1960, (6), 117–123; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D129.—The optimum conditions for a determination are described. To determine H in titanium, excite spectra by impulse discharges in air from a condenser of 800 μF capacitance at 220 V; a 50-μH inductance is introduced into the discharge circuit. The H line at 6563 A is compared with the background. The determination of N is carried out in a CO_2 medium at a pressure of 300 torr. Spectra are excited in a low-voltage spark from a 400-μF condenser at 220 V; the inductance of the discharge circuit is 10 μH. The N line at 3995 A is compared with the background. The effect of Ca on the intensity of the N line is studied. In the case of iron, copper, chromium and tungsten, sparking in CO_2 leads to an impoverishment of the electrode nitrogen; this is not observed with titanium and vanadium. A determination of O in metals is carried out with a low-voltage discharge spark in H with a condenser of capacitance 400 μF, at 400 V with an inductance of 5 μH. A good sensitivity is obtained for O in industrial titanium samples; O is determined under the same conditions in chromium steel from the O line at 4596·13 A, which is compared with the background. K. R. Cook

4469. **Indirect potentiometric determination of zinc, silver, indium and halogens with quinol.** J. Blažek, J. Doležal and J. Zýka (Anal. Chem. Inst., Charles' Univ., Prague, Czechoslovakia). *Z. anal. Chem.*, 1961, **180** (4), 241–246 (in German).—Zinc, Ag and In may be determined by the addition of an excess of 0·1N-$K_3Fe(CN)_6$ in weakly acid soln. and titration with 0·1N-quinol. The liberated $[Fe(CN)_6]^{4-}$ are consumed by the Zn, Ag or In until the reaction is complete, when a sudden change in potential is observed. Bromine, Cl, ClO^-, BrO^- or BrO_3^- may be estimated by addition of $K_4Fe(CN)_6$ and titration of the $K_3Fe(CN)_6$ formed with 0·1N-quinol. T. R. Andrew

4470. **Anion-exchange separation of zinc, cadmium, copper, lead, bismuth and silver.** M. N. Zvereva and N. I. Vinogradova. *Vestn. Leningr. Univ.*, 1961, No. 10, *Ser. Fiz. i Khim.*, (2), 142–144.—The anion-exchange resin EDE-10P can be used for the quant. separation of Zn, Cu, Cd, Pb, Bi and Ag, *e.g.*, as mixed chlorides. A column 10 to 13 mm in diam. containing 10 g of EDE-10P (particle size 0·25 to 0·5 mm) is used with flow-rates of 1 to 2 ml per min. Copper is eluted with 2M-HCl, Zn with 0·65M-HCl, Cd with 0·25M-HCl, Pb with H_2O, Bi with 5M-H_2SO_4 and Ag with 3M-aq. NH_3. A. Burwood-Smith

4471. **Derivatives of 1,4-dihydroxyanthraquinone as colorimetric reagents for the determination of aluminium, beryllium and thorium.** E. G. Owens, II. *Dissert. Abstr.*, 1960, **21** (5), 1038.—2-Phenoxyquinizarin-3,4′-disulphonic acid (dipotassium salt) is used for the titration of Th with EDTA (disodium salt) at pH 1·6 to 3·4. Quinizarin-2-sulphonic acid (sodium salt) yields a stable violet complex with Al in methanol soln. which can be measured at 560 mμ. Some interfering ions (not Be^{2+}, Sc^{3+}, Th^{4+}, Ti^{4+}, Y^{3+}, Zr^{4+}, F^-, PO_4^{3-} and rare-earth metals) are removed by electrolysis at a mercury cathode; 0·01 to 1·0% of Al can be determined in bronze and steel. 2-Phenoxyquinizarin-3,4′-disulphonic acid (disodium salt) is used for the spectrophotometric determination of Be (0·1 to 0·7 p.p.m. in the soln.) at 550 mμ in beryl, aluminium metal, copper alloys, bronze and steel. The Ca salt of EDTA masks most interfering ions, but not Cr^{3+}, F^-, Mg^{2+}, PO_4^{3-}, Th^{4+} or Zr^{4+}. Large amounts of interfering ions can be removed by ion exchange on Amberlite IR-120 or by electrolysis. With Ca - EDTA plus Cd - EDTA as masking agent, both Be and Al can be determined with an accuracy of ±2·5% for Be and ±10% for Al. R. E. E.

4472. **Anion-exchange separation of tin, antimony, lead and copper.** M. Ariel and E. Kirowa (Dept. of Chem., Israel Inst. of Technol., Haifa). *Talanta*, 1961, **8** (4), 214–222 (in English).—Tin- or lead-based alloys are dissolved in conc. HCl with the addition of H_2O_2 (30%). When dissolution is complete the excess of H_2O_2 is removed by boiling and the Sb is reduced by the addition of Na_2SO_3 soln. An aliquot of this soln. is placed on the top of a column of Amberlite IRA-400 and washed in with 7N-HCl, and the column is eluted with small vol. of 7N-HCl to remove Pb, 1·56N-HCl to remove Cu, N-HF containing HCl to remove Sb, and 6N-NaOH to remove Sn. The method is rapid, allowing four parallel determinations to be carried out in 2 hr., and showed a recovery of ⩽98% of each metal present in synthetic mixtures and alloys. G. S. Roberts

4473. **Separation of small amounts of bismuth, lead, cobalt, nickel, phosphorus, iron and copper with ion-exchange resins.** V. Stepin, V. I. Ponosov and E. V. Silaeva. Publ.: "Khromatografiya ee Teoriya i Primenenie," Akad. Nauk SSSR, Moscow, 1960, 230–235; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D43.—The method is based on the ability of the elements being separated to form anionic chloride complexes, the stability of which is a function of the pH of the medium. Carry out determinations on columns (50 cm × 0·7 cm) filled with anion-exchange resin (Cl^- or H^+ form). To separate small amounts of Bi from Cu, Fe, Pb, Co and other elements, pass the test soln. through a column of TM anion-exchange resin; wash the column with 4N-HCl followed by 0·02N-HCl; Mn, Ni, Cr, Co and other components pass into the percolate but Bi remains on the column as an anionic complex. Elute the Bi with 2N-H_2SO_4 and determine it as the iodide complex. To recover Pb from tin, zinc or high-duty steel alloy, use a column of TM anion-exchange resin, which adsorbs Pb from 0·5N to 0·8N-HCl. Elute the Pb with 0·02N-HCl and determine it by dithizone titration. To determine Co in high-purity nickel or antimony, use the method of Moor and Kraus (*J. Amer. Chem. Soc.*, 1952, **75**, 1460). To determine Ni in antimony or its alloys, pass the test soln., in 8N-HCl, through a column of anion-exchange resin (AN-2F); Ni, which

does not form anionic complexes, passes through and is determined with dimethylglyoxime. To determine Fe in nickel, antimony or lead, dissolve the metal in 8N-HCl and pass the soln. through a column of anion-exchange resin (AN-2F). Wash the column with 6N-HCl, and elute Cu plus Fe with 0·5N-HCl. Convert both cations in the eluate into pyrophosphate complexes, adjust the pH to 10 or 11 and pass the soln. through a column of Wofatit R; only Fe passes into the percolate. Elute the Cu with HCl (1:4) and determine it photometrically by the diethyldithiocarbamate method. To determine P in pure metals or steel, pass the test soln. through cation-exchange resin and determine P in the percolate photometrically by the molybdenum blue method. This method can be used to determine such cations as Bi, Pb, Fe and Cu in a single sample of tin. Pass the test soln. (0·5N in HCl) through a column containing TM anion-exchange resin; Cu and Fe pass into the percolate, but Pb and Bi remain on the column. Elute the Pb with 0·02N-HCl and the Bi with 2N-H_2SO_4; convert the Fe and Cu into pyrophosphate complexes and then proceed as described above. K. R. Cook

4474. **High-frequency titration as applied to the determination of thorium, uranium, sulphate and free acid. I–V.** O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. CF-59-5-72, 1959. 20 pp.—In Part I, the reproducibility of the method for the titration of standard soln. that contained 50 mg of Th, in the absence of interferences, is established. Under these conditions, the coeff. of variation of the method was <1%. In Part II, the effect of U on the high-frequency titration of Th, as well as the application of the method to actual samples, is discussed. Uranium can be tolerated when the ratio of U to Th is 5:1. When the method is applied to the analysis of representative samples, the coeff. of variation is 1%. Attempts to determine U by high-frequency titration with 8-hydroxyquinoline were unsuccessful. Tests on this titration and possible reasons for its failure are discussed in Part III. The application of the high-frequency titration method to the determination of SO_4^{2-} in soln. of uranyl sulphate is described in Part IV. The coeff. of variation, on titrating 40 to 70 mg of SO_4^{2-} with $BaCl_2$ after the U is masked with citrate or F^-, is 2%. In Part V, the high-frequency titration of free acid in soln. of uranyl sulphate is discussed. Uranium in amounts up to 350 mg, which was the highest level tested, does not interfere. The coeff. of variation is ≃2%.
Nucl. Sci. Abstr.

4475. **Successive determination of iron, aluminium, manganese, calcium and magnesium by EDTA titration.** Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *Japan Analyst*, 1960, **9** (3), 238–243.—When the successive EDTA titration method is to be applied to the analysis of slags, back-titration with $CuSO_4$ in the presence of a known excess of EDTA and 1-(2-pyridylazo)-2-naphthol (**I**) is the recommended procedure for Al, Mn, Ca and Mg. Iron in a mixture in HCl, or in $HClO_4$, is titrated at pH 2·0 with salicylic acid as indicator. The pH of the soln. is adjusted to 3·0, then an excess of EDTA soln. and **I** are added and the soln. is back-titrated with $CuSO_4$, for Al. Then Mn is similarly titrated at pH 4·5. A part of this titrated soln. is adjusted to pH 10·0, and is similarly back-titrated for the sum of Ca and Mg. Calcium oxalate is pptd. in the remainder of the soln. and the Mg is titrated similarly. K. Saito

4476. **Separation of hydrogen, deuterium and hydrogen deuteride mixtures by gas chromatography.** P. P. Hunt and H. A. Smith (Chem. Dept., Univ. Tennessee, Knoxville, U.S.A.). *J. Phys. Chem.*, 1961, **65** (1), 87–89.—The separation has been satisfactorily achieved on a column of Cr_2O_3 deposited on alumina (*cf.* Smith and Hunt, *Ibid.*, 1960, **64**, 383) partially de-activated with water, at 77° K with Ne at 25 to 35 ml per min. as carrier gas. The preparation of the column is described and elution curves are given for activated, partially de-activated and de-activated columns. Curves are also given for columns of silica gel at 77° K with H as carrier gas at 144 ml per min. (separation of H^3H and $^3H_2$), at 112° K with He at 58 ml per min. (H_2 and $^3H_2$), at 112° K with He at 60 ml per min. (H_2, H^3H and $^2H_2$) and at 112° K with Ne at 25 ml per min. (H_2 and $^3H_2$), and for a charcoal column at 77° K with H at 75 ml per min. (H^3H and $^3H_2$).
R. E. E.

4477. **Gas chromatography of parahydrogen, orthohydrogen, hydrogen deuteride and deuterium.** Shozo Furuyama and Takeo Kwan (Chem. Dept., Fac. Sci., Hokkaido Univ., Sapporo, Japan). *J. Phys. Chem.*, 1961, **65** (1), 190–191.—The separation is described of mixtures of hydrogen isotopes (0·3 to 0·9 ml) on two columns in series, the first (200 cm × 0·4 cm) containing active alumina and the second (50 cm × 0·4 cm) containing active alumina coated with ferric oxide (Moore and Ward, *Ibid.*, 1960, **64**, 832), with He at 65 to 69 ml per min. as carrier gas. The separated isotopes were burned in a combustion tube at 450° before passing to the thermal-conductivity detector. Four peaks, with retention times ranging from 6 to 10 min., were obtained, corresponding to the four isotopes. Recoveries from two known mixtures were satisfactory. R. E. E.

4478. **Determination of very small amounts of hydrogen peroxide.** H. Perschke and E. Broda (Inst. f. phys. Chem., Univ. Wien, Austria). *Nature*, 1961, **190**, 257–258.—Concn. of 10^{-12} to 10^{-10} mole of H_2O_2 per ml in water can be determined, to within ≃10%, by using the reaction reported by Andreae (*Anal. Abstr.*, 1955, **2**, 2797), *viz*, the stoicheiometric oxidation of scopoletin (7-hydroxy-6-methoxy-1,2-benzopyrone) (**I**) by H_2O_2 in the presence of horse-radish peroxidase (**II**), with loss of fluorescence. The sample soln. (0·1 ml) is mixed with soln. of **I** and **II** (0·1 ml of each) and, 15 min. later, 0·15M-borate buffer (pH 10) (0·3 ml) is added. Exactly one-half of the mixture is then transferred to a platinum dish and the residual fluorescence is measured in a Galvanek-Morrison fluorimeter against a reagent blank and compared with the original fluorescence of **I**. The concn. of **I** and **II** are not critical, but specially purified water (prep. described) must be used in the preparation of the soln. The method is especially suitable for determining the biological effects of small concn. of H_2O_2, *e.g.*, produced by irradiation of cell-cultures with γ-rays (5 to 10 r). W. J. Baker

4479. **Indicator tube for the rapid determination of hydrogen peroxide vapour in air.** L. A. Mokhov and N. S. Mareeva. USSR Pat. 134,057 (10.12.1960).—The tube contains silica gel that has been impregnated with an ethanolic $Ti(SO_4)_2$ soln. and air-dried [to 1 g of pure silica gel ignited at 600° to 700°, of

grain size $>0{\cdot}25$ to $0{\cdot}35$ mm, add 2 ml of a 2% ethanolic $Ti(SO_4)_2$ soln., and stir until dry]. The indicator is packed in a tube (8 mm long × 3 mm internal diam.) in a layer of <3 to 4 mm between glass-wool pads. The indicator turns yellow when air containing H_2O_2 is drawn through it; the vol. of air passed up to the colour change is measured, and the H_2O_2 content is found from a calibration curve (given) of H_2O_2 concn. *vs.* vol. of air passed. The method can be used to determine $0{\cdot}005$ to $0{\cdot}1$ mg of H_2O_2 per litre, 600 ml of air being passed through the tube. Relative humidities of 35 to 85% and temp. $<35°$ do not affect the determination.

C. D. KOPKIN

4480. **Direct photo-electric determination of lithium in ores.** A. G. Krest'yaninov, Yu. I. Stakheev and Ya. D. Raĭkhbaum. "Spektr. Anal. v Tsvet. Metall.," M., Metallurgizdat, 1960, 87–94; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D37.—*Procedure*—Mix the sample with a buffer mixture (1 : 1) of charcoal powder and Na_2CO_3. Treat the buffer with an ethanolic rosin soln. to stabilise the rate of entry of the powder into the discharge. Excite spectra in a 15-amp. a.c. arc, introducing the powder into the arc by an air jet so that the material enters the discharge at the rate of 600 mg per min.

K. R. COOK

4481. **Flame-photometric determination of sodium in potassium dichromate used as a primary standard.** Ichiro Toyama and Keiichi Takauchi (Osaka Ind. Res. Inst., Oyodo-ku, Osaka). *Japan Analyst*, 1960, **9** (2), 123–127.—Interference due to Cr in the determination of Na is eliminated by decreasing the slit width to $0{\cdot}015$ mm. The background intensity in the region 582 to 593 mμ is then practically constant, and the intensity of the Na line at 589 mμ is proportional to concn. of Na $<1{\cdot}0$ p.p.m., when the concn. of $K_2Cr_2O_7$ is $<0{\cdot}5\%$. K. SAITO

4482. **Volumetric analysis of sodium in brine associated with natural gas.** Shigeo Iwata (Gov. Chem. Ind. Res. Inst., Hatagaya, Shibuya-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 178–179.—When Na^+ are pptd. with magnesium uranyl acetate, no other ions in the brine are co-pptd. The ppt. is digested with ammonium buffer (pH 10) to extract Na and Mg, and the Mg^{2+} are titrated with EDTA. The error is $<1{\cdot}5\%$ for 4 to 11 mg of Na. K. SAITO

4483. **Studies on chemical analysis by the use of organic reagents. III. Photometric determination of copper with 1,2-di-(o-aminobenzylideneamino)-ethane.** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *Japan Analyst*, 1960, **9** (3), 202–206.—A $0{\cdot}01\%$ soln. of 1,2-di-(*o*-aminobenzylideneamino)ethane in benzene reacts with Cu (<60 μg) at pH >8 and the Cu is transferred to the org. layer. The extinction of that layer at 412 mμ is proportional to the concn. of Cu (<6 μg per ml). Iron (<1000-fold) is masked by tartrate, and Ni and Co by EDTA. Gold, Ag, Hg and large amounts of Zn, Cd and Pb interfere.

K. SAITO

4484. **Determination of copper in sulphuric acid by square-wave polarography.** Yoshikazu Yasumori and Tadashi Eguchi (Yanagimoto Co., Kiya-machi, Nakagyo-ku, Kyoto). *Japan Analyst*, 1960, **9** (2), 127–131.—Copper gives a characteristic wave in H_2SO_4 of concn. <5M; O and SO_2 must be absent. The temp. coeff. is $\simeq 3\%$ per degree, and 50° seems to be the optimum temp. The working curve is not linear, but is reproducible between $0{\cdot}1$ and $1{\cdot}0$ mg of Cu per litre. K. SAITO

4485. **Studies on electrolytic analysis in the presence of a chelating agent. IV. Determination of copper in the presence of bismuth, antimony and arsenic by the use of a tartrate - DTPA electrolyte.** Genkichi Nakagawa (Ind. Chem. Dept., Nagoya Inst. Tech., Gokiso-cho, Showa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 102–104.—Diethyltriaminepenta-acetic acid (DTPA) complexes of As^V and Bi do not give deposits at $-0{\cdot}60$ V *vs.* the S.C.E., whereas those of As^{III} and Sb^{III} give slight deposits. By the use of a Na tartrate soln. (0·2M) of pH 4·5 containing DTPA (2 × the quantity required to complex Bi + As + Sb) and hydroxyammonium chloride (2 g per 100 ml), Cu ($\simeq 100$ mg) is deposited quant. within 90 min. at $-0{\cdot}40$ to $-0{\cdot}45$ V. K. SAITO

4486. **Separation and determination of trace amounts of gold in copper by extraction with ethyl acetate.** Shizo Hirano, Atsushi Mizuike and Koji Yamada (Fac. of Engng, Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1960, **9** (2), 164–167.—The extraction of Au (3 to 10 μg) from 10% HCl soln. with ethyl acetate is not affected by HNO_3, and Sandell's method with *p*-dimethylaminobenzylidenerhodanine (**I**) can be satisfactorily applied to 0 to 6 μg of Au. Silver ($<0{\cdot}1$ mg), Fe and Hg (<1 mg each) do not interfere. The error is $<10\%$ for 2 to 500 p.p.m. of Au in copper, and the time taken for a determination is <5 hr. *Procedure*—Dissolve the sample (1 g) in HNO_3 (1 : 1) (8 ml) and conc. HCl (1·5 ml). Filter if a large amount of Ag is present. Dilute the soln. to decrease the concn. of Cu to 1 g per 15 ml of 2·7N acid containing 1·2M-Cl^-. Extract with ethyl acetate (2 × 15 ml) and wash the combined org. layers with 1·2N-HCl. Evaporate the extract to dryness, dissolve the residue in aqua regia and dilute to 25 ml. Determine Au in an aliquot with **I** at 562 mμ.

K. SAITO

4487. **Approximate evaluation of the factors influencing the concentration dependence of the intensity of copper lines in the excitation of the spectra of some alloys in an a.c. arc.** N. K. Rudnevskiĭ and Yu. S. Kalinin. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kiĭ*], 1960, (2), 257–262; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D35.—The changes of temp., concn. and degree of ionisation of copper atoms in the gas cloud of the arc affect the dependence of the intensity of the spark and arc lines on the copper content of the alloys; Cu - Ni and Cu - Mn alloys containing 1·2 to 79% of Ni and 5·2 to 32·2% of Mn were studied. The degree of ionisation of the copper atoms in the arc cloud was found experimentally, for which purpose a special mixture was evaporated from a carbon electrode, and the degree of ionisation of magnesium atoms was determined from lines of Mg II and Mg I with known probabilities of transitions; the temp. was found from the relative intensity of the Cu lines. Together with results from other studies, this enabled the dependence of the intensities of the spark and arc Cu lines on its content in the alloy to be determined. Analysis of the resulting data showed that the intensities of the lines due to copper ions when the spectra of Cu - Ni and Cu - Mn alloys are excited in an a.c. arc are mainly determined by the entry of the material of these alloys into the arc plasma, and by the change of its temp.

and the change of the degree of ionisation of copper atoms. (26 references.) C. D. KOPKIN

4488. **Electrochromatographic separation of silver and thallium ions from each other and from mixtures of various polyvalent cations.** H. H. Strain, J. F. Binder, G. H. Evans, H. D. Frame, jun., and J. J. Hines (Argonne Nat. Lab., Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 527–531.—The separation of Ag and Tl from each other by electrochromatography has been studied with a variety of potentially complexing basal soln. Work was carried out on silver soln., thallium soln., a mixture containing Ag and Tl, and a mixture containing Ag, Al, Ba, Cd, Ce, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Tl and Zn. In a basal soln. of 0·05M-HCN, 0·05M-ammonium oxalate and 0·185M-aq. NH_3, Tl is separated from Ag and from the other cations in the mixture, which remain bunched together. In 0·0125M-nitrilotriacetic acid - 3M-aq. NH_3, Ag is separated from the other cations. T. R. ANDREW

4489. **Spectrographic method for the quantitative determination of low-concentration impurities in high-purity fine silver.** A. J. Lincoln and J. Kohler (Res. and Dev. Div., Engelhard Industries Inc., Newark, N.J., U.S.A.). *Engelhard Industries Tech. Bull.*, 1960, **1** (3), 103–105.—A Stallwood jet (*Anal. Abstr.*, 1954, **1**, 1736) surrounding the electrodes and an inert gas were used to increase the sensitivity and decrease the background in a d.c. arc procedure. The electrodes were of graphite and the jet was used with Ar at a flow-rate of 4 litres per min. Samples were converted into $AgNO_3$ and used as a dry powder. Analytical lines, silver lines and concn. ranges (p.p.m.) are given for 22 metals. G. RUSSELL

4490. **Application of the decomposition of the sample by hydrofluoric acid with the fluorescent morin method to the determination of small amounts of beryllium in ores and minerals.** L. P. Tsareva. *Soobshch. Dal'nevost. Fil. Sibirsk. Otdel., Akad. Nauk SSSR*, 1960, **12**, 137–139; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D65.—The finely ground sample (0·3 g) in a platinum dish is covered with water, 1 to 1·5 ml of H_2SO_4 and 4 to 6 ml of HF are added and the soln. is evaporated to dryness and cooled; 1 ml of H_2SO_4 is added and the soln. is again evaporated to complete the removal of HF. The dry residue is heated with 5% H_2SO_4 until completely dissolved and the soln. is then analysed as in the original method [*Ref. Zhur., Khim.*, 1958, (15), Abstr. No. 49,989]. The present method takes 1 to 1·5 days as compared with 3 to 3·5 days for the original method. A. BURWOOD-SMITH

4491. **Photometric determination of beryllium in bronze.** L. O. Matveev and I. S. Mustafin. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 217–222; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D80.—At pH 6·5 to 8, quinizarindisulphonic acid (**I**) forms coloured complexes with Be^{2+} (max. absorption at 530 mμ) and several other ions. The determination of Be is little affected by the presence of Al; Cu is masked with $Na_2S_2O_3$ soln., which also reduces the influence of Fe. *Procedure*—Dissolve the sample (0·1 to 0·15 g) in 10 ml of HNO_3 (1:1), evaporate the soln. to dryness on a water bath, add 2 to 3 ml of HCl (1:1), again evaporate to dryness, dissolve the residue in 40 to 50 ml of water (dissolving any residual turbidity in a few drops of HCl), and make up to 100 ml. To 0·5 ml of the resulting soln. add 0·5 ml of 7% $Na_2S_2O_3$ soln., 3 ml of buffer soln. of pH 6·96 to 7·03 (mix a soln. of 8·24 g of barbitone sodium in 1 litre with 177 ml of 0·2N-HCl, adding a few crystals of thymol to stabilise the soln.) and 1 ml of 0·08% **I** soln. Heat the soln. on a water bath at 60° to 70° for 5 min., cool, and measure the extinction at 530 mμ in a 0·5-cm cell. For 2·12 to 2·57% of Be the error varies from +0·40 to +3·77%. C. D. KOPKIN

4492. **Separation of beryllium from aluminium, tervalent iron, yttrium, cerium, and the rare-earth metals by cation-exchange chromatography.** F. W. E. Strelow (Nat. Chem. Res. Lab., C.S.I.R., Pretoria, S. Africa). *Anal. Chem.*, 1961, **33** (4), 542–545.—Beryllium is quant. retained on a column of Dowex AG-50W-X8 resin from soln. $\geq$0·3N in cations (including H^+). It may be subsequently eluted with 1·0N-HCl or 1·2N-HNO_3, the latter eluent giving a cleaner separation from Fe^{III}. Iron, followed by Al, is eluted with 2N-HCl, and 3N-HCl is used to elute Y and Ce, in that order. Some bivalent Co, Ni, Mn, Cu, Zn and Mg, and Ti^{IV}, is eluted with Be, and Cd, Sn^{IV}, Se, Hg^{II}, V^{V}, Mo^{V}, Au^{III}, As^{III}, Sb^{III}, Bi^{III} and Pt^{IV} can be eluted with 0·5N-HCl before the Be. Interference from the heavy metals is not serious in the assay of beryllium ores and a separation with aq. NH_3 is frequently adequate. As an example of this procedure, the determination of Be in gadolinite is described. T. R. ANDREW

4493. **Analysis of beryllium and beryllium oxide. VI. Determination of tantalum and niobium.** J. O. Hibbits, H. Oberthin, R. Liu and S. Kallman (General Electric Co., Nuclear Propulsion Dept., Cincinnati, Ohio, U.S.A.). *Talanta*, 1961, **8** (4), 209–213 (in English).—Niobium and Ta are pptd. from a HCl - H_2SO_4 soln. by cupferron, with Zr as collector. A soln. of HCl and HF containing the Nb and Ta, together with interfering elements pptd. with them by the cupferron, is passed through an anion-exchange column (Dowex 1-X8). Only the Nb and Ta and some Sn are retained. Niobium is then eluted with a soln. of HF and NH_4Cl and Ta with a soln. of NH_4F and NH_4Cl. The two metals are again pptd. with cupferron with Zr as collector. The Nb is determined spectrophotometrically with quinol in conc. H_2SO_4. The soln. is stable for at least 24 hr., and the extinction, which is a linear function of concn. up to 4 μg per ml, is measured at 395 or 490 mμ. The pyrogallol complex of Ta in ammonium citrate - ammonium oxalate - H_2SO_4 soln. is measured similarly at 398 or 420 mμ and gives a rectilinear calibration up to 12 μg of Ta per ml. No interference was caused by additions of 10-mg amounts of 68 elements. The accuracy is ±5% or 10 μg (whichever is greater) for Nb and ±10% or 30 μg for Ta. G. S. ROBERTS

4494. **Increasing the sensitivity of certain colour reactions for magnesium.** Ya. I. Korenman. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1960, (2), 307–313; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D81.—Methods for increasing the sensitivity of reactions for the detection of very small amounts of Mg^{2+} with magneson I (*p*-nitrophenylazo-resorcinol), magneson II (*p*-nitrophenylazo-1-naphthol), Titan yellow, quinalizarin, Eriochrome black T, Acid Chrome dark blue (C.I. Mordant Blue 7) and 5-*p*-nitrophenylazoanthranilic acid (magneson III) are studied. It is shown that prolonged standing after the addition of the reagents considerably increases the sensitivity of the reactions,

standing for 1 day increasing the sensitivity by two orders of magnitude; in the case of magneson III, standing for 8 days increases it 1000 times. Heating on a boiling-water bath for 15 min. does not increase the sensitivity, nor does flotation of the reaction products with water-immiscible solvents (isopropyl ether, toluene, cyclohexane, $CHCl_3$, ethyl bromide, bromobenzene, dibutyl phthalate, nitrobenzene, aniline, etc.). Addition of water-miscible solvents (acetone, isopropyl alcohol) in reactions with Chromogen black, quinalizarin and Titan yellow increases the sensitivity of detection of Mg by one order of magnitude; this is not observed with the other reagents. A study of the behaviour of these reagents and the corresponding reaction products in alkaline medium towards H_2O_2 and Br has shown that the use of oxidising agents does not increase the sensitivity to Mg. C. D. KOPKIN

4495. **Metallochromic indicators. X. A new mixed indicator for the chelatometric determination of calcium.** V. Svoboda, V. Chromý, J. Körbl and L. Dorazil (Spolana, N.E., Res. Centre of Lachema Plant, Brno, Czechoslavakia). *Talanta*, 1961, **8** (4), 249–252 (in English).—It has been found possible to improve the indicating properties of fluorescein complexan by mixing it with one quarter of its wt. of phenolphthalein complexan. In this ratio the two indicators correct certain undesirable features in each other. The mixed indicator does not produce better end-points in the presence of interfering cations, except Na. G. S. ROBERTS

4496. **Spectrophotometric determination of calcium with glyoxal bis-(o-hydroxyanil).** T. M. Florence and J. Morgan (Atomic Energy Commission Res. Est., Lucas Heights, N.S.W., Australia). *Australian Atomic Energy Comm.*, Rep. AAEC/E-60, 1961. 4 pp.—A selective method is described for the spectrophotometric determination of Ca with glyoxal bis-(*o*-hydroxyanil) as the chromogenic agent. A comprehensive study of interferences and reagent variables was made. NUCL. SCI. ABSTR.

4497. **Complexometric determination of calcium and magnesium in ferromanganese slags.** A. G. C. Morris (Feralloys Ltd., P.O. Box 21, Cato Ridge, Natal, S. Africa). *Anal. Chem.*, 1961, **33** (4), 599–602.—Weigh 0·5 g of sample into a 500-ml conical beaker, add 10 to 15 ml of H_2O and boil. Remove from the source of heat, add 50 ml of conc. HNO_3 and swirl until the sample has dissolved. Heat the soln. to boiling, add $KClO_3$ (3 g in small portions) and boil vigorously until the vol. is reduced to <25 ml, then add 25 ml of cold water and cool rapidly. Filter off the ppt. of MnO_2 and dilute the filtrate to 250 ml. To a 100-ml portion add KOH soln. (25%) to give a pH of 1·5 to 2·0 and then 33% triethanolamine soln. (20 ml). If necessary adjust the pH to 9 to 10 by further additions of triethanolamine. Add KOH soln. (25%) until the pH is $\simeq$13, and titrate Ca with 0·05M-EDTA (disodium salt), with fluorexone as indicator. Treat a second 100-ml portion similarly, adding aq. NH_3 - NH_4Cl buffer soln. in place of the final addition of KOH to achieve a pH of 10. Titrate Mg plus Ca, with thymolphthalexone {3,3′-bis[*NN*-di(carboxymethyl)aminomethylthymolphthalein]} as indicator. Results on samples containing $\simeq$30% of CaO and $\simeq$5% of MgO agree well with those obtained by gravimetric methods. T. R. ANDREW

4498. **Simultaneous determination of calcium, magnesium and sulphate in gypsum by ethylenediaminetetra-acetic acid.** D. Prakash and D. N. Tewari (Directorate of Geol. and Mining, Uttar Pradesh, Lucknow, India). *Z. anal. Chem.*, 1961, **180** (4), 268–270 (in English).—Calcium and Mg are determined in 25 ml of a 0·2% soln. of the sample by conventional EDTA methods. Sulphate is determined in 25 ml by the addition of 25 ml of 0·02M-$BaCl_2$, the ppt. is coagulated by boiling and, after addition of aq. NH_3 - NH_4Cl buffer and KCN soln., the excess of Ba, together with the Ca and Mg, are determined by EDTA titration. T. R. ANDREW

4499. **Complexometric determination of calcium and magnesium in manganese ores.** J. Jankovsky (Inst. f. Erzforsch., Prague, Czechoslovakia). *Z. anal. Chem.*, 1961, **180** (5), 330–338 (in German).—After removal of SiO_2, sesquioxides and PO_4^{3-} by pptn. with aq. NH_3, Mn is pptd. at pH 9 with Na diethyldithiocarbamate and the ppt. is extracted with $CHCl_3$ containing 3% of ethyl acetate. Calcium and Mg are determined in the aq. phase by EDTA titration. T. R. ANDREW

4500. **Complexometric determination of calcium, magnesium and manganese when present together.** V. A. Rad'ko and E. M. Yakimets. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 176–181; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D47.—The method is based on the EDTA titration of Ca plus Mg plus Mn, titration of Ca after Mg and Mn have been pptd. as $Mg(OH)_2$ and MnS, and titration of Mn^{2+} after Ca^{2+} and Mg^{2+} have been pptd. by fluoride in an ammoniacal - acetate medium; Mg is determined by difference. To determine Ca plus Mg plus Mn add 5% hydroxyammonium chloride soln. (5 ml) to an aliquot of the soln., neutralise with 5% aq. NH_3 to methyl orange, dilute with H_2O to 100 ml, add ammoniacal buffer soln. (5 ml), Acid Chrome dark blue (C.I. Mordant Blue 7) soln. (5 or 6 drops) and slowly titrate with EDTA (disodium salt) until the colour changes from red to blue. To determine Ca^{2+} neutralise an aliquot (10 to 25 ml) of the soln. to methyl orange, add Na_2S - NaOH soln. (a mixture of equal vol. of 10% soln) (10 ml), set aside for 3 to 5 min. and titrate with EDTA soln. To determine Mn^{2+} neutralise an aliquot of the soln. with 5% aq. NH_3 soln. to methyl orange, dilute to 80 ml, add ammoniacal - acetate buffer soln. (5 ml) at pH 8·5 to 9·0, NH_4F soln. (30 g of NH_4F in 70 ml of H_2O) (10 ml) and titrate with EDTA soln. K. R. COOK

4501. **Determination of calcium, strontium, barium and potassium in the binder of microcrystalline phosphor layers.** J. Toperczer (Staatl. Onkolog. Inst., Budapest, Hungary). *Z. anal. Chem.*, 1961, **180** (4), 265–268 (in German).—Results are presented for the determination of Ca, Ba, Sr or K in zinc sulphide or zinc silicate screens by flame-photometric, spectrographic and radio-active tracer methods. The tracer method (described) has advantages in sensitivity. T. R. ANDREW

4502. **X-ray fluorescence analysis using ion-exchange resin for sample support. Determination of strontium in decimolar calcium acetate solutions.** R. L. Collin (Cancer Res. Inst., New England Deaconess Hospital, Boston, Mass., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 605–607.—Solutions may be examined by passage through a column of cation-exchange resin, removal and pressing of the resin

into a disc and X-ray fluorescence analysis of the disc. An internal standard is added to the soln. and this overcomes possible errors. The determination of Sr (20 to 1000 μg) in 0·1M-Ca acetate (10 ml) with RbCl as internal standard is given as an example. T. R. ANDREW

4503. **Cation-exchange behaviour of strontium on Dowex 50W-X8. Separation from mixtures.** S. K. Majumdar and A. K. De (Dept. of Chem., Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (4), 356–359 (in English).—Strontium can be quantitatively recovered by elution with 2 to 4M-HNO_3, 3 to 4M-HCl, 3 to 4M-NH_4Cl, 2 to 3M-$NaNO_3$ and 2M to 4M-ammonium acetate. Strontium was separated from Cu^{2+}, Hg^{2+}, Cs^+, Zn^{2+}, Cd^{2+} and U^{6+} by selective elution with 4M-HCl. It was also separated from Zr^{4+}, Th^{4+}, Fe^{3+} and Bi^{3+} with the help of complexing agents such as EDTA and citric acid. A. J. BENNETT

4504. **Colorimetric determination of zinc.** V. M. Dziomko, I. G. Shafran, K. A. Dunaevskaya, K. Z. Zonenberg, K. E. Kalinina and V. A. Oboznenko. USSR Pat. 135,682 (15.2.1961).—The reagent used is 2-(8-amino-1-hydroxy-3,6-disulpho-2-naphthylazo)-2′-hydroxy-5′-methylazoxybenzene (**I**), which with Zn gives a blue complex with a max. absorption at 595 mμ (555 mμ for **I**) with a second max. at 450 mμ (400 mμ for **I**). The complex is stable up to 35°, and the colour is stable at room temp. for at least 7 days. The sensitivity is 0·02 μg of Zn in 5 ml of soln. No interference in the determination of 2 μg of Zn is caused by up to 50 μg of Na, Mg, K, Ca, V^V, Cr^{VI}, Rb, Mo^{VI}, Cd, Tl, Cs, Ba, Hg^I, Hg^{II} or Pb, and practically no interference by 0·5 μg of Be, Ce, Fe, Ni or Sc; 2 μg of Cu; 3 μg of Nd or Sb; 6 μg of Mn; 7 μg of Pd; 8 μg of Sn; 10 μg of Se, Pt^{II} or Zr; 30 μg of Al; 40 μg of Bi; or 50 μg of Ti, Ru or Hf. To determine Zn in high-purity HCl, evaporate 50 ml to dryness in a platinum or quartz dish on a water bath, dissolve the residue in 1·5 ml of water, transfer the soln. to a colourless glass tube, dilute to 2·5 ml with borate - alkali buffer (pH 10·5), mix, add 1 ml of 0·005% **I** soln., mix, and after 5 min. compare the colour with that of standards. C. D. KOPKIN

4505. **Photometric determination of zinc with xylenol orange.** K. Študlar and I. Janoušek (Res. and Test Inst., Škoda, V. I. Lenin Works Plzeň, Czechoslovakia). *Talanta*, 1961, **8** (4), 203–208 (in English).—The properties and production of the Zn - xylenol orange complex have been studied. In the optimum pH range (5·8 to 6·2) a stable red complex containing 1 mol. of Zn and 1 mol. of xylenol orange is formed. The max. difference in extinction between complex and reagent is reached at 570 mμ and at concn. up to 100 μg per 50 ml the Beer - Lambert law holds. The method has been applied to the determination of 0·01 to 0·5% of Zn in bronze; in this case it has been found essential to separate Cu and Pb by electrolysis, followed by removal of Al, Fe, Ni and Mn on a strongly basic ion-exchange column. G. S. ROBERTS

4506. **Determination of zinc in metallurgical materials by atomic-absorption spectrophotometry.** J. A. F. Gidley and J. T. Jones (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1961, **86**, 271.—In previous work (*Ibid.*, 1960, **85**, 249) it was reported that soln. of HCl caused considerable absorption at the wavelength of the zinc resonance line (2138 A) and also at wavelengths between 2000 and 2200 A. Further work has now shown that the interference was avoided when the acid was neutralised with NaOH but not with aq. NH_3, and that the hollow-cathode emission lines used for absorption measurements in the region 2000 to 2200 A were ground-state copper lines derived from the reaction between the surface-oxide layers of the brass hollow-cathode burner and HCl or NH_4Cl, the reaction products being carried into the flame. Other workers have detected no interference when stainless-steel or aluminium burners are used. A. O. JONES

4507. **Thermometric titrations of zinc, cadmium and mercuric salts.** M. P. Ben-Yair. *Trans. Chalmers Univ. Technol., Gothenburg*, 1961, (236), 11 pp.—When a soln. in a Dewar flask is titrated with another soln., the initial temp. of which is 1° higher than that of the soln. in the flask, at a constant rate of 1 ml per min., the temp. of the reaction mixture, measured by a Beckmann thermometer, varies continuously until the end-point is reached, when a sharp change takes place in the slope of the curve of Beckmann reading *vs.* vol. of titrant added. In general, 200 ml of test soln. (0·01 to 0·05M) is titrated with M-aq. reagent. The method is not affected by gel-formation, precipitation or turbidity. Graphs are given for the titration of $HgCl_2$ with aq. NH_3 (point of inflection corresponding to a ratio of Hg to NH_3 = 1:1), of $Cd(NO_3)_2$ and $Zn(NO_3)_2$ with NaOH and of NaOH with $Cd(NO_3)_2$ and $Zn(NO_3)_2$ (Cd or Zn:OH = 1:2). Results are also given for the titration of $Cd(NO_3)_2$ and $Zn(NO_3)_2$ with aq. NH_3 (Cd or Zn:OH = 1:2). With $Zn(NO_3)_2$ a second break was also obtained in this case, corresponding to Zn:OH = 1:10. A manual procedure was adopted here, but a suitable automatic apparatus has been described (Jordan and Alleman, *Anal. Chem.*, 1957, **29**, 9). R. E. E.

4508. **Analysis of zinc alloys. Rapid determination of aluminium, iron, copper, cadmium and lead.** R. J. Gajan and D. M. Geehan. *Metal Ind.*, 1961, **98** (16), 319–320.—*Cf. Rep. Invest. U.S. Bur. Min.*, 1961, No. 5727; *Anal. Abstr.*, 1961, **8**, 3614. J. W. PRICE

4509. **Separation of zinc and cadmium with anionites.** M. N. Zvereva and R. Ya. Abdrakhmanov. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 46–52; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D48.—The method is based on adsorption on the anionite PE-9 or EDE-10P (Cl^- form) and elution with HCl of various concn. Max. adsorption of the halide complexes of Zn and Cd takes place from 2N-HCl; under these conditions, Fe, Co, Ni, Ti, Cr, Mn, Al and Cu are not adsorbed. There is practically no adsorption of Zn on EDE-10P from 0·5N-HCl, but considerable amounts of Cd are adsorbed. For the separation, pass the sample (> 50 ml, with 2 g-equiv. of HCl per litre) at a rate of < 2 ml per min. through 10 g of PE-9 or EDE-10P (grain size 0·25 to 0·5 mm), wash the resin with 200 ml of 0·5N-HCl and determine Zn in the percolate with EDTA (disodium salt) or by pptn. with Na_2CO_3. Then elute Cd with 200 ml of 0·005N-HCl or 200 ml of water, and determine it by titration with EDTA (disodium salt) or gravimetrically as the pyrophosphate. By this method, Zn can be separated not only from Cd, but also from group-2 cations and from Cu, which are not adsorbed on PE-9 or

EDE-10P from 2N-HCl. In this case pass the soln. (2N in HCl) through 10 g of anionite (Cl^- form), and elute all cations except Zn and Cd with 150 ml of 2N-HCl; then selectively elute first Zn and then Cd with the soln. mentioned above. The method successfully separates Zn and Cd at ratios from 10:1 to 1:10, in the presence of 50 mg of Cd or Cu, Mn, Al, Fe, Ni and Co. C. D. KOPKIN

4510. **Co-precipitation of microgram amounts of zinc and gallium with calcium phosphate.** Yu. V. Morachevskiĭ and V. N. Zaĭtsev. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 77–80; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D2.—Gallium and Zn^{2+} are quant. co-pptd. with $Ca_3(PO_4)_2$ from soln. containing 0·05 mole of NH_4NO_3 per litre at pH > 8·5 and 6 to 9, and from soln. containing 5 moles of NH_4NO_3 per litre at pH 5 to 7·5 and > 6, respectively. Based on the different conditions for the co-pptn. of Ga^{3+} and Zn^{2+} with $Ca_3(PO_4)_2$, a method is developed for the separation of Ga^{3+} from a 1000-fold excess of Zn^{2+}. By co-pptg. Ga^{3+} at pH 7·5 from soln. containing 5 moles of NH_4NO_3 per litre, Zn^{2+} remain in soln. For the complete separation of Ga and Zn, the ppt. is dissolved in a little dil. HNO_3 and the co-pptn. of Ga^{3+} is repeated under the same conditions, after which the Ga^{3+} are extracted from the ppt. with aq. NH_3. C. D. KOPKIN

4511. **Spectrographic analysis of high-purity zinc after concentration.** D. M. Shvarts, L. N. Kaporskiĭ and I. S. Nilova. "Spektr. Anal. v Tsvet. Metall.," M., Metallurgizdat, 1960, 107–124; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D107.—The method is based on the difference between the vapour pressure of the impurities and the main components of the sample. Carry out the concentration in a hard glass tube connected to a condenser. Place the zinc (4 to 5 g) at the bottom of the tube, evacuate to $\simeq 4 \times 10^{-3}$ torr and place it in an oven at 500°; the evaporated Zn condenses in the condenser and a film of ZnO is formed. The impurities Cu, Bi, Sn, Ni, Pb, Fe, Al and Sb remain in the tube. Prepare standards by mixing zinc with oxides of the impurities or by fusion of zinc with metals. Place the enriched samples in the crater of a graphite electrode, excite spectra in an a.c. arc and photograph them in a medium spectrograph. Construct a calibration curve. The error is $\simeq 25\%$. K. R. COOK

4512. **Determination of cadmium and bismuth by a simplified internal electrolysis diaphragm method.** A. K. Zhdanov and U. Kh. Khodzhaeva. *Uzb. Khim. Zhur.*, 1960, (5), 46–52; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D60.—Moderate and large amounts of Cd and Bi can be determined by the internal electrolysis method in a simplified electrolyser with a large-pore glass diaphragm. To determine Cd (up to 250 mg in 250 ml) there are used an acetate buffer soln. (pH 5·2), a zinc anode in 20% KCl soln., and a platinum grid as cathode. With < 100 mg of Cd in 250 ml the electrolysis can also be carried out with a soln. of Na citrate (3 g of salt), Na tartrate (3 g of salt) and an oxalate buffer mixture (10 g of ammonium oxalate and 2 to 2·5 g of oxalic acid). To separate Bi (up to 100 mg) from a soln. of vol. 250 ml there may be used a soln. of acetic acid (5 ml of conc. acid) and H_3BO_3 (1 g), a soln. containing Na tartrate (3 g), sucrose ((15 g and hydrazine (1·2 g), a soln. of Na citrate and a soln. containing 4 g of EDTA (disodium salt) and 10 ml of HNO_3. As anodes are used iron or zinc plates immersed in 5% $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln., 10% K_2SO_4 soln. or 20% KNO_3 soln. With > 100 mg of Bi in 250 ml, good results are obtained with a soln. of EDTA (disodium salt) or citrate. The electrolysis of Cd and Bi is carried out at 50° to 80°, with stirring. C. D. KOPKIN

4513. **Study of the entry of the material of a cadmium - zinc alloy into the inter-electrode gap under the action of a spark discharge.** N. K. Rudnevskiĭ, A. I. Dryakhlov and V. S. Trofimov. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kiĭ*], 1960, (1), 58–63; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D36.—The earlier method (*Ref. Zhur., Fiz.*, 1959, (7), Abstr. No. 16,709, 16,711) was used to study the entry of a Cd - Zn alloy into the discharge gap of a condensed spark. The spectrum was excited from the spark between identical electrodes of binary Cd - Zn alloys in the form of rods of diam. 8 mm shaped to a hemisphere. It was shown that there is no linear relationship between the amount of substance entering the discharge gap and the concn. of Cd (or Zn) in the alloy if the whole range of concn. from 0 to 100% is considered. There are only separate sections of linearity, the extent of which increases after sparking for 5 min. The introduction of Zn into cadmium electrodes or of Cd into zinc electrodes increases the rate of entry of the material of the alloy into the discharge gap. The introduction of 20% of Zn into cadmium electrodes increases the rate of entry by 1·4 times, and the introduction of 5% of Cd into zinc electrodes by 1·7 times. The concn. of Cd and Zn in the material entering the spark gap from the electrodes is practically the same as their concn. in the alloys. Sparking for up to 5 min. does not change these proportions. The relationships between the "absolute" intensities of the spectrographic lines Cd 3261·06, Cd 2748·58, Zn 3282·33 and Zn 2557·96 A and the content of Cd or Zn are in accordance with data on the entry of these elements into the discharge gap. There is a linear relationship between the relative intensity of the lines Cd 2748·58 and Zn 2557 A and the atomic concn. in the alloy for the whole range from 0 to 100%, both for the alloys and for the products entering the spark gap. C. D. KOPKIN

4514. **Amperometric titration of mercury with EDTA using a tantalum electrode.** V. A. Khadeev and A. T. Bazarbaev. *Uzb. Khim. Zhur.*, 1960, (5), 38–45; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D75.—A method is given for the direct amperometric titration of Hg^{2+} with EDTA (disodium salt) (**I**) in a medium of 0·25N to 0·5N-H_2SO_4 or HNO_3, with a rotating tantalum electrode. The titration is not hindered by large amounts of HF, acetic, tartaric or citric acid, Co, Ag, Zn, Cd, Ni, U, Al, Ti, Th, Ba or Sr, or by 25 times the amount of Cr and Pb. Large amounts of Pb, Cr, V, Mo and Fe^{3+}, and Cl^- and Cu interfere. The influence of Mo in the titration soln. is overcome by the addition of 0·5 g of Na tartrate, and Fe^{3+} by the addition of 1 g of $Na_4P_2O_7$. It is possible to determine both Hg^{2+} and Ag by beginning the titration with **I** at +1·2 V (determination of Hg^{2+}) and then with KI at +0·8 V (determination of Hg^{2+} and Ag) in the presence of other elements. A. BURWOOD-SMITH

4515. **Spectrophotometric determination of boron with methyl violet.** Isao Muraki, Kazuo Hiiro, Hideko Fukuda and Eimei Miyade (Osaka Ind. Res. Inst., Ooyodo-ku, Osaka). *Japan Analyst*, 1960, **9** (2), 71–78.—Poluéktov's methyl violet (**I**) method (*Zhur. Anal. Khim.*, 1958, **13**, 396) was improved by the use of $NH_4F.HF$ and HCl in place of HF and with glycine as buffer. The max. error decreased from 4·2 to 1·9%. The sample soln. is mixed with 0·5 ml each of M-$NH_4F.HF$, 0·2N-HCl and 0·02M-glycine, made up to 3·0 ml, and heated in a boiling-water bath for 15 min. The product is cooled, then shaken with benzene (4 ml) and **I** soln. (0·2% in water, 1·0 ml) for >10 sec. and the extinction of the org. layer is measured at 610 mμ within 10 min. K. SAITO

4516. **Photometric determination of boron in zirconium and its alloys with niobium.** P. N. Palei, A. A. Nemodruk and Z. I. Pŷzhova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 223–230; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D109.—The sample (5 to 500 μg, depending on the B content) is fused with 0·5 to 5 g of $Na_2S_2O_7$ in a silica dish at 410° to 450°. After cooling, the melt is dissolved in 25 ml of H_2O and conc. H_2SO_4 is added to give a vol. of 50 ml. To 0·1 to 1·5 ml of this soln., enough H_2SO_4 (1:1) is added to make the vol. 1·5 ml, followed by 10 ml of quinalizarin tetra-acetate (**I**) soln. (20 mg of quinalizarin is dissolved in 750 ml of conc. H_2SO_4 and 250 ml of acetic acid added). The soln. is shaken, set aside for 15 to 20 min. and measured in a 1-cm cell at 620 mμ, against a mixture of 10 ml of **I** soln. with 1·5 ml of H_2SO_4 (1:1). Results are referred to a calibration graph. The colour obeys Beer's law for concn. of B ≯ 1·4 μg per ml. For mixtures containing 0·01 to 0·05% of B, errors are ≯5%, at higher concn. of B (<10%) the error is 3%. A. BURWOOD-SMITH

4517. **Determination of boron in ferro-boron.** Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *Japan Analyst*, 1960, **9** (1), 22–26.—The gravimetric determination of B with tartrate and Ba^{2+} (Gautier and Pignard, *Z. anal. Chem.*, 1952, **135**, 417) was applied to the analysis of ferro-boron. Although the composition of the ppt. is uncertain, the molar ratio of Ba to B remains constant on ignition, the empirical formula being Ba_3BO_6. Small amounts of Si and Al (2 mg each), Cr, Mo and V do not interfere. *Procedure*—Fuse the sample (0·5 g) with Na_2O_2 (5 g) at 800° for 3 min. Dissolve the melt in hot water (100 ml), boil for 2 min. and make up to 250 ml (together with the ppt.). Filter through dry paper and neutralise a 25-ml portion with HCl to methyl red, add HCl (1:1, 0·5 ml), NH_4Cl soln. (20%, 10 ml), tartaric acid soln. (5%, 10 ml) and $BaCl_2$ soln. (5%, 10 ml), adjust the pH to 8·6 to 9·2 and cool to below 20°. Filter off the ppt. after 10 min., wash it with cold water, ignite at 700° to 800° and weigh. K. SAITO

4518. **Spectrographic determination of traces of boron in graphite for nuclear reactors.** Tokunosuke Nakajima, Masao Takahashi and Masutaka Morishita (Japan Atomic Energy Res. Inst., Tokyo). *J. Atomic Energy Soc. Japan*, 1961, **3**, 104–109 (in Japanese).—Two procedures are described for the spectrographic determination of 0·002 to 3 p.p.m. of B in graphite. In the first method, preliminary concentration is carried out by the removal of graphite by ashing in the presence of La_2O_3. Then the B in the La_2O_3 is determined by the carrier-distillation method. In the second method, a sample in the form of powder is compressed into pellets with the aid of a phenol - formaldehyde resin as binding medium, and the pellets are arced at 7 amp. d.c. By means of display microphotometry, the peak height of B at 2497·73 A is compared with that of the NO(γ) band component at 2497·14 A. NUCL. SCI. ABSTR.

4519. **Study of decaborane by infra-red spectroscopy.** Mlle. Le Sech and M. P. Garrigues. *Chim. Anal.*, 1961, **43** (4), 174–177.—The i.r. spectrum of decaborane (**I**) has been studied and compared with the spectra of pentaborane and diborane. The sample of **I** was analysed by dispersing the solid in liquid paraffin and compressing the soln. between KBr plates. The structure of **I** is discussed and five characteristic bands at 718, 763, 858, 1008 and 1551 cm^{-1} are noted. It is suggested that a quant. determination may be made by dissolving **I** in CS_2 and using the peak at 718 cm^{-1}. R. A. HENDEY

4520. **Comparison of methods for the determination of traces of aluminium with organic reagents.** L. A. Molot, I. S. Mustafin and N. S. Frumina. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 231–242; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D81.—Methods for the photometric determination of Al^{3+} with haematoxylin, 8-hydroxyquinoline, Alizarin red S, aluminon and stilbazo are critically studied, and the main properties of the complexes formed are tabulated. Haematoxylin and 8-hydroxyquinoline are not recommended for the determination of Al in industrial materials, particularly steel; for steel, the most useful reagents are Alizarin red S and aluminon, used together with thioglycollic acid. The methods are simple and give accurate and reproducible results. The possible use of stilbazo as a reagent for the photometric determination of Al is indicated. C. D. KOPKIN

4521. **Studies on chemical analysis by the use of organic reagents. II. Gravimetric and volumetric determination of aluminium with *NN'*-ethylenedianthranilic acid.** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *Japan Analyst*, 1960, **9** (3), 199–202.—*NN'*-Ethylenedianthranilic acid reacts with Al in a molar ratio of 3:1 and the resulting ppt. is ignited to give Al_2O_3. The optimum pH of the reaction is 4 to 5. There is no interference from Na^+, Cl^-, NO_3^-, SO_4^{2-} or acetate (<0·4 g each). The error is <0·7%. The ppt. is dissolved in a mixture of 6N-HCl and ethanol (1:1) and titrated with 0·1N-$KBrO_3$, with indigo carmine as indicator. The error is <2%. Tervalent Fe, Zn, Cr and Cu must be removed beforehand. K. SAITO

4522. **Determination of alkalis in alumina by sintering with boric acid: X-ray diffraction and emission spectrographic analysis of the residue.** Kazunobu Kodama and Hajime Shiio (Nagoya Municipal Ind. Res. Inst., Atsuta-ku, Nagoya). *Japan Analyst*, 1960, **9** (2), 161–164.—When the sintering method of Archibald and McLeod (*Anal. Chem.*, 1952, **24**, 222) is carried out carefully with good mixing of alumina and borax (1:3), <20% of the alumina remains crystalline and contains <0·10% of Na. K. SAITO

4523. **Fluorescence determination of scandium, gallium and zirconium on paper chromatograms, with β-resorcylaldehyde formylhydrazone.** Z. Holzbecher (Inst. for Anal. Chem., Chem. Tech. Coll., Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (4), 1204–1206 (in German).—The soln. of metal salts is placed on a filter-paper strip and developed with n-butanol - ethyl acetate - 35% HCl (2:2:1), then dried and treated with a 0·01% soln. of the reagent in ethanol. The chromatogram is examined under u.v. light (366 mμ). Scandium and Ga appear as blue fluorescent strips and Zr forms a bluish-green spot, maximum intensity being obtained after a few minutes. The lower limit of detection is 0·04 μg of Sc, 0·06 μg of Ga and 0·5 μg of Zr. The method is sensitive and highly selective in the presence of a large number of other metals. Determinations of Al, Zn and Be can be carried out by exposing the chromatograms to NH_3 vapour.

R. PRESSER

4524. **Fluorescence determination of gallium in complex ores and their processing products.** S. M. Milaev. *Sb. Trud. Vses. Nauch.-Issled. Gorn.-Metallurg. Inst. Tsvet. Met.*, 1959, (5), 41–45; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D84.—It is shown that the determination of Ga by measuring the intensity of fluorescence of an ether soln. of its 8-hydroxyquinoline complex, which has been used for the analysis of dusts from lead, zinc and copper production (Gur'ev *et al.*, *Anal. Abstr.*, 1956, **3**, 3300), can be applied to complex ores and their processing products. The influence of Fe^{III}, which is partially extracted with the Ga by the ether, is completely removed by adding 0·2 to 0·5 ml of 15% $TiCl_3$ soln. to the test soln. C. D. KOPKIN

4525. **Separation of small amounts of gallium from aluminium by co-precipitation.** Yu. V. Morachevskiĭ, V. P. Zaltsev and V. V. Fokin. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 81–84; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D49.—Aluminium in concn. of 0·5 to 250 μg per ml is quant. pptd. with $Ca_3(PO_4)_2$ at pH 8·5 from soln. containing ≃2·5 moles of NH_4Cl or NH_4NO_3 per litre, while Ga^{3+} remain completely in soln. at pH >7·5 and with 2·5 moles of NH_4NO_3 per litre. A method is developed for the separation of 25 μg of Ga from 300 mg of Al, comprising the pptn. of Ga on partially pptd. $Al(OH)_3$ and the separation of the Ga from the Al by co-pptn. of the Al with $Ca_3(PO_4)_2$. To 50 ml of sample soln. add 2·5 to 5·0 g of NH_4Cl, heat, and add 0·5N-aq. NH_3 until the soln. is slightly turbid. Filter off the ppt., wash it with water and dissolve it on the filter in hot dil. HCl. Evaporate this soln. to 1 to 2 ml, add 10 ml of 5N-NH_4Cl, $Ca(NO_3)_2$ soln. (= 20 mg of Ca), $(NH_4)_2HPO_4$ soln. and 10 ml of conc. aq. NH_3. Filter off the ppt. and wash it with 40 ml of a mixture (1:1) of conc. aq. NH_3 and 5N-NH_4Cl. Evaporate the filtrate, add rhodamine B which, with $GaCl_4^-$, forms a coloured complex, extract the complex with a mixture (5:1) of benzene and ethyl ether, and measure the extinction of the extract. The method can be used for the determination of Ga in bauxite. C. D. KOPKIN

4526. **Spectrographic determination of trace impurities in gallium.** J. H. Oldfield and E. P. Bridge (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Analyst*, 1961, **86**, 267–269.—The sample, after removal of surface contamination by acid treatment, is weighed and dissolved in 10 ml of HCl in a polytetrafluoroethylene beaker, 1 ml of 0·01N-H_2SO_4 being added and the liquid heated on a silica hot-plate. The soln. is evaporated to ≃5 ml and 10N-HCl (5 ml) is added. The normality of the soln. is determined by diluting 0·1 ml with 5 ml of water and titrating with 0·1N-NaOH, 4·6 ml being deducted from the titre on the assumption that $Ga(OH)_3$ is pptd. The acid concn. is then adjusted to 8N, the final vol. being 10 to 15 ml. The soln. is shaken with 15 ml of isopropyl ether in a polyethylene bottle and centrifuged, the ether layer is removed and the acid concn. of the aq. layer is again determined and, if necessary, adjusted to 7·5N. A second extraction is made similarly and the acid extract is filtered through quartz wool, the filtrate being collected in a platinum crucible, evaporated to fuming with H_2SO_4 and then again evaporated after addition of $CuSO_4$ soln. The residue is dissolved in 0·1 ml of water and transferred to a graphite electrode and excited as previously described (*Ibid.*, 1960, **85**, 97). Results of recovery tests and impurity determinations are quoted.

A. O. JONES

4527. **Studies of the solvent extraction of indium oxinate.** G. K. Schweitzer and G. R. Coe (Dept. of Chem., Univ. of Tennessee, Knoxville, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (4), 311–315 (in English).—The extraction of radio-labelled In from aq. soln. into organic solvents containing 8-hydroxyquinoline was investigated. The presence of complexing agents forming water-soluble complexes with In caused shifts in the pH at which 50% extraction occurred ($pH_{\frac{1}{2}}$). In the absence of such masking agents the $pH_{\frac{1}{2}}$ was the same at 0° and 30°. The shift of $pH_{\frac{1}{2}}$ by different organic solvents was <1·6. A. J. BENNETT

4528. **Separation of indium from aluminium by extraction as dibutylammonium indium sulphide.** M. Ziegler (Anorg.-Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1961, **180** (5), 348–350 (in German).—Copper, Au^{3+}, Hg_2^{2+}, MoO_4^{2-}, As^{3+}, Pt^{4+}, Ge^{4+}, Zn^{2+}, Cd^{2+} and In^{3+} can be extracted as complex dibutylammonium sulphides into dichloromethane, achieving good separation from Al. *Procedure for In*—To the weakly acid soln., containing >40 mg of In, is added 8 ml of di-*n*-butylamine and 10 ml of di-*n*-butylamine polysulphide soln. (prepared by passing H_2S into a cooled mixture of 200 g of methanol, 130 g of di-*n*-butylamine and 32 g of sulphur powder until the sulphur has dissolved), and the whole is well mixed and extracted with 30 ml of dichloromethane. After separation of the phases, the aq. layer is treated with a further 2·5 ml of di-*n*-butylamine and 5 ml of di-*n*-butylamine polysulphide soln. and extracted with a further 20 ml of dichloromethane. Indium may be pptd. as sulphide by acidification of the organic extract with HNO_3 and, after 5 min., making weakly alkaline with aq. NH_3, boiling, and setting aside for 2 hr.; Al can be pptd. from the aq. phase as hydroxide.

T. R. ANDREW

4529. **Spectrographic determination of indium, thallium and germanium in dusts from lead production and their sulphation products.** L. S. Bortnik. *Sb. Trud. Vses. Nauch.-Issled. Gorn.-Metallurg. Inst. Tsvet. Met.*, 1959, (5), 196–201; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D153.—For the determination of In and Tl, prepare a buffer mixture of 1 part of

PbO_2 and 2 parts of NaCl, containing 30% of $CdSO_4$. Mix the sample with the buffer in the ratio 1:2. Excite the spectra in an a.c. arc (5 amp.) with evaporation of the sample for 40 sec. from a groove in a carbon electrode of diam. and depth 4 mm. Photograph the spectra in a medium spectrograph. Determine In and Tl in the concn. range 0·001 to 0·05% from the lines In 3256·09 and Tl 3519·24 A, and in the range 0·005 to 0·2% from the lines In 3258·56 and Tl 3529·49 A, with Cd 3252·52 A as comparison line. The mean error of the analysis is ±10%. Use carbon powder as buffer in the determination of Ge. Excite the spectra at 9 amp. and photograph for 30 sec. The lines used are Ge 2691·3 and Ga 2659·9 A for ≃0·01%; the error is ±10%. Prepare standards on a base of the sulphate product. C. D. KOPKIN

4530. **Studies on alternating-current polarography. III. Determination of lead, cadmium and zinc in indium.** Hideko Shirai (Inst. Ind. Sci., Tokyo Univ., Yayoi-cho, Chiba). *Japan Analyst*, 1960, **9** (3), 206–209.—In M-H_3PO_4 containing 0·5M-HNO_3, the peak waves of Cd, Pb and Zn are not affected by an ≃50-fold molar excess of In. The peak height is proportional to the concn. of these ions for <0·25 millimole. Halide ions vitiate the determination. K. SAITO

4531. **Extractive separation of thallium from accompanying elements with melts of diphenylamine.** G. K. Pel'sh and V. I. D'yachkov. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 102–108; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D50.—The extraction of Tl^{3+} with melts of diphenylamine (**I**) from soln. of varying acidity containing NH_4Cl, NH_4Br or KI is studied. It is shown that Tl^{3+} are 99·6% extracted from 2N-HCl containing excess of KI, with a distribution coeff. of 270. In the presence of an excess of EDTA (disodium salt) (**II**), a single extraction can separate Tl^{3+} (>1 mg) from 200-fold amounts of Pb^{2+}, Zn^{2+} or Cd^{2+} and 300-fold amounts of Cu^{2+} and Fe^{3+}. Double extraction is necessary for 98% extraction of Tl^{3+} into the org. phase in the presence of 1000-fold amounts of accompanying ions. To 1 to 2 ml of test soln. add conc. HCl till the acid concn. is 2N, then 1 ml of 20% KI soln. and 2·5 to 3·0 g of **I**; place the tube in a bath of hot water and shake for 1 min. After separation of the layers, wash the solidified org. layer with water, add excess of **II** soln. and again heat to melt the **I**. Neutralise the soln. to methyl red and add ammoniacal buffer soln. The Tl^{3+} pass into the aq. phase and are determined by titration of the excess of **II**. C. D. KOPKIN

4532. **Separation of thallium by radial paper chromatography.** G. V. Efremov and A. F. Vetoshkina. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 53–57; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D51.—This technique is used to separate Tl^{3+} from similar amounts of Fe, Cu, Ni and Co. Best results were obtained by using n-butanol satd. with N-HCl as solvent; the R_F values obtained were Tl 1·0, Fe 0·17, Cu 0·07, and Co and Ni 0·06. The paper is first treated with a mixture (9:1) of acetone and conc. HCl, to remove traces of Fe. The chromatogram is cut into 4 sectors. One is used to determine the positions of the zones, with $K_4Fe(CN)_6$ for Fe and Cu, dimethylglyoxime for Ni, 1-nitroso-2-naphthol for Co, and dithizone for Tl. The Tl zones are cut out and boiled for 2 to 3 min. with 25 ml of 0·4N-HCl. The soln. is filtered and made up to a known vol. with 0·4N-HCl, and Tl is determined colorimetrically in an aliquot with methyl violet. Complete separation of Tl is not achieved, because of the reduction of Tl^{3+} during their movement on the paper, the influence of Ni^{2+} and Co^{2+} of low mobility, which decrease the rate of movement of Tl^{3+}, and the presence of insufficient solvent in the chromatography of more than 100 μg of Tl. C. D. KOPKIN

4533. **Co-precipitation of thallium with the thiourea complex of lead.** G. V. Efremov and N. E. Karyagina. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 71–76; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D87.—The co-pptn. of Tl^+ with a ppt. of $2Pb(NO_3)_2.11CS(NH_2)_2$ is studied. It is shown that Tl^+ are completely co-pptd. with a 25 to 5000-fold excess of Pb^{2+} from soln. containing ≃1 mole of HNO_3 per litre by adding an equal vol. of a satd. soln. of thiourea in N-HNO_3. After dissolving the ppt. in hot water, Tl^+ are separated from most of the Pb^{2+} by pptg. the Pb^{2+} with 0·5N-K_2SO_4. The filtrate is adjusted to a pH of 9 to 12 with aq. NH_3, and Tl^+ are extracted with a $CHCl_3$ soln. of dithizone. The Tl is re-extracted from the org. phase with 0·4N-HCl and oxidised with bromine water to Tl^{3+}; methyl violet is added to form a coloured complex with $TlCl_4^-$, and the extinction of the soln. is measured. The method described can be used to separate Tl from Hg and Sb, and for the determination of $1·6 \times 10^{-5}$ % of Tl in natural chlorides and brines. C. D. KOPKIN

4534. **Coulometric determination of thallium with electrolytically generated chlorine.** V. K. Khakimova and P. K. Agasyan. *Uzb. Khim. Zhur.*, 1960, (5), 31–37; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D79.—The conditions are studied for the coulometric titration of Tl^+ with electrolytically generated Cl produced at a platinum electrode. It is shown that, by potentiometric control of the end-point, 51 to 1125 μg of Tl^+ can be determined in 20 ml of HCl with errors of ±4·4 to 1·2 μg. A. BURWOOD-SMITH

4535. **Polarographic determination of thallium in an atmospheric sample.** A. S. Landry (Intern. Co-operation Admin., Lima, Peru). *Amer. Ind. Hyg. Ass. J.*, 1960, **21**, 407–413.—Thallium is determined in the presence of Pb by a polarographic method, with 2·7M-$CaCl_2$ as a supporting electrolyte and EDTA (disodium salt) as a chelating agent. Lead in concn. >20 μg per ml does not interfere with the determination of 10 to 50 μg of Tl per ml. In the presence of Fe, the Tl must be extracted from N-HBr with ethyl ether. The Pb can be determined simultaneously with the Tl. CHEM. ABSTR.

4536. **Quantitative spectrochemical determination of rare-earth elements.** P. A. Koka and Z. A. Chirkina. "Dokl. Mezhvuz. Nauch. Konferensil po Spektroskopil i Spektr. Anal., "Tomsk, Tomsk Univ., 1960, 33–35; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D80.—The total rare-earth elements are determined by a method involving chemical separation from their ores and minerals. The separated elements are diluted with 10 to 30 parts of calcium silicide and mixed with graphite powder (1:1). The silicide sharply increases the sensitivity of the determination. The mixture is evaporated from a graphite electrode. Elements of the Ce

group are determined from lines in the range 4200 to 4600 A, those of the Y group from 3000 to 3500 A; Sc serves as comparison element. Tables of analytical lines are given. Thorium is determined together with the rare-earth elements. The error is within ± 12%. A. BURWOOD-SMITH

4537. **Separation of heavy rare-earth elements by reversed-phase partition chromatography.** I. Fidelis and S. Siekierski (Dept. of Radiochem., Inst. Nucl. Res., Warsaw, Poland). *J. Chromatography*, 1961, **5** (2), 161–165 (in English).—Radioactive rare-earth metals from Tb to Lu can be separated by chromatography with tributyl phosphate as the stationary phase and HNO_3 as the mobile phase. The columns are prepared by a method previously described (Siekierski and Fidelis, *Anal. Abstr.*, 1961, **8**, 966). The best separation, in a convenient elution-time, is given by 12·3M-HNO_3; the peaks corresponding to Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu are completely resolved. For the elution of the heavier rare-earth metals (Tb, Er, Tm, Yb and Lu), 11·8M- or 12·3M-HCl can be used, but the partition coefficients of the lighter rare-earth metals are too small even in the most conc. HCl soln. The shape of the elution curve varies with the concn. of the rare-earth metal, and becomes asymmetric and broad if the concn. is too high.
R. M. ROWLEY

4538. **Use of acetic acid in the chromatographic separation of yttrium and cerium.** A. I. Subbotina. *Trudy Khim. i Khim. Tekhnol* [*Gor'kiĭ*], 1960, (1), 30–32; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D52.—The method is based on adsorption of the mixture on the resin KU-2 (H^+ form) from HCl soln., with subsequent elution of the components with acetate buffer mixtures. The test soln. (pH 2·0) is added to the column (diam. 15 mm, height 22 cm) which is washed with water till free from Cl^-, and the eluents, containing 1·0M to 1·5M-acetic acid (**I**) at pH 4 to 5, are passed. With 1·5M-**I** at pH 4·4 there is no separation, and at pH 4·1 and 4·2 the elution curves overlap. If the column is eluted with 1·0M-**I** at pH 4·4 there is a clear separation, but if the pH is increased to 4·6 to 4·8 the separation is not so satisfactory. With 1·25M-**I** there is partial elution of the components at pH 4·3. If the **I** concn. is decreased from 1·5 to 1·0M, the vol. of eluent required for the desorption of Y and Ce increases. In all cases first Y and then Ce is eluted. C. D. KOPKIN

4539. **Colorimetric determination of cerium in magnesium alloys.** V. N. Tikhonov. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 124–133; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D89.—A study is made of the effect of the pH, the amount of H_2O_2 and the amount of EDTA (**I**) on the determination of Ce in magnesium alloys by the oxidation reaction between H_2O_2 and the Ce^{3+} complex; the colour of the Ce^{4+} complex is measured photometrically. It is shown that when **I** is present in an ammoniacal medium in an amount insufficient to combine with the Mg, a constant value for the extinction of the soln. is reached more rapidly than in the absence of Mg. The optimum pH is 9·6 to 10·0 and the optimum amount of H_2O_2 is 7 to 11 drops of a 5% soln. for 0·1 to 1·0 mg of Ce. A determination of 0·5 mg of Ce in the presence of 50 mg of Mg and 1 ml of 0·05M-**I** is not affected by the presence of 0·5 mg of Mn, or of 1 mg of Mn in the presence of 2 ml of **I** soln. or of > 6 mg of Mn in the presence of 8 to 10 ml of **I** soln. The interference of Fe^{3+} is avoided by extracting the Fe^{3+} as a thiocyanate with isoamyl alcohol (the excess of SCN^- is oxidised with conc. HNO_3). The effect of rare-earth elements, in reducing the intensity of colour of the Ce complex, is overcome by means of the method of addition. K. R. COOK

4540. **Determination of cerium-144 in reactor fuel processing and effluent treatment plant solutions.** U.K.A.E.A. (Production Group, Tech. Branch, Windscale, Cumberland, England). U.K.A.E.A. Report PG 205(W), 1961. 8 pp.—Full experimental details are given. The Ce, with added carrier, is oxidised with Pb_3O_4 to Ce^{IV} and extracted into a mixture of tributyl phosphate and CCl_4 (1:1) and then into hydroxyammonium chloride soln. After pptn. of ^{234}Th as iodate, with Zr as carrier, and centrifuging, the Ce in the supernatant liquid is pptd., first as the hydroxide and then as the oxalate, which is β-counted through an aluminium absorber (159 mg per sq. cm). The coeff. of variation is 10%.
G. J. HUNTER

4541. **Near infra-red spectral absorption of praseodymium.** Masahito Mamiya (Gov. Chem. Ind. Res. Inst., Hatagaya, Shibuya-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 177–178.—When the i.r. absorption of Pr is measured in a mixture of water and dioxan (1:1), a peak is observed at 1600 mμ; this is not shown by other rare-earth elements (Pm, Er, Tm, Yb and Lu were not examined). K. SAITO

4542. **Polarographic determination of ytterbium.** Akio Iwase (Fac. of Liberal Arts, Yamagata Univ., Koshirakawa-cho, Yamagata). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 95–98.—Ytterbium gives two reduction waves at −1·448 ± 0·002 V and −2·046 ± 0·002 V *vs.* the S.C.E. at pH 3·4 to 6 in LiCl or tetraethylammonium bromide (**I**). The first wave corresponds to the reduction of Yb^{III} to Yb^{II} and the second to Yb^{II} to Yb. The second wave gives a max. the height of which increases with increase in concn. of Yb. The limiting current of the first wave decreases at pH > 6, whilst that of the second wave decreases at pH < 4. For quant. analysis by means of the first wave, 0·1M-**I** containing 0·01% of gelatin is the best supporting electrolyte, the pH being adjusted to 5·6 with LiOH. For the second wave, 0·05M-LiCl of pH 3·4 is suitable. Interference results from a 50-fold excess of Nd, a 100-fold excess of La and a 10-fold excess of Sm. K. SAITO

4543. **Liquid scintillation counting of carbon-14. Use of ethanolamine - 2-methoxyethanol - toluene.** H. Jeffay and J. Alvarez (Dept. of Biochem., Univ. of Illinois, Chicago, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 612–615.—The method consists in the oxidation of ^{14}C to $^{14}CO_2$ and then trapping the gas as the ethanolamine carbonate in 2-methoxyethanol. An aliquot of the carbonate soln. is added to toluene containing 2,5-diphenyloxazole as a scintillator, cooled to 0° and counted. The method may be used with small or large samples of CO_2, and 16 oxidations can be completed in a morning.
C. B. BAINES

4544. **Automatic scanner device for the determination of carbon-14 on paper chromatograms.** M. Dubini and R. Fanteschi. *Comit. Nazl. Ricerche Nucleari CNI-32*, 1960. 11 pp. (in English).—An apparatus is described for the detection and recording of the activity of ^{14}C-labelled compounds on

chromatographic paper strips. A flow-type proportional counter provided with a narrow window of 1·2 mg per sq. cm is used. The paper is wrapped over the surface of a cylinder rotating in front of the counter slit. Rotation speeds are varied by using cylinders of various diameters. Spots with edges as little as 3 mm apart can be distinguished. The smallest detectable activity is 4×10^{-4} μC. For activities ranging from 4×10^{-4} to 6×10^{-2} μC, a relation exists between the activity of the spots and the area of the corresponding peaks on the recording paper. CHEM. ABSTR.

4545. **Radioactivation analysis by the use of short-lived nuclides. II. Simultaneous determination of vanadium and aluminium in graphite.** Toshio Nakai, Seishi Yajima, Minoru Okada, Koreyuki Shiba and Terutomi Maki (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 104–107. —For the identification and quant. determination of ^{52}V (0·1 to 1000 p.p.m. of V), produced by neutron activation of graphite, γ-ray scintillation spectrometry of its 1·44-MeV γ-ray is more useful than the conventional β-ray counting. With the aid of a well-type NaI crystal (diameter 1·75 in.) the peak is distinguished from that of ^{28}Al (1·78 MeV). Only negligible amounts of ^{56}Mn, ^{24}Na, ^{99m}Mo, ^{65}Ni and ^{42}K are produced. Since the photo-peak of ^{41}Ar (produced from air) vitiates the estimation of V, the irradiated sample must be transferred rapidly to a counting vessel. The error is within ± 10% for 0·1 p.p.m. of V.

K. SAITO

4546. **Detection and determination of cyanide ions with mercuric diphenylcarbazide paper.** Yoshimasa Tanaka and Setsu Yamamoto (Fac. of Pharm., Kumamoto Univ., Oe-cho). *Japan Analyst*, 1960, **9** (1), 8–12.—Blue-violet mercuric diphenylcarbazide paper changes to red in the presence of CN^- (>0·25 μg per 0·05 ml) in a neutral or weakly basic soln. With gaseous HCN flowing in a thin glass tube, the length of colour change on a strip of paper is proportional to the amount of CN^- (< 10 μg). The sample (≃1 ml) is heated in a glass tube (diameter 15 mm, length 50 mm) with $NaHCO_3$ (0·5 g). The error is <5%. Interference from $[Fe(CN)_6]^{4-}$ is avoided by the use of $Cd(NO_3)_2$ mixed with the $NaHCO_3$. K. SAITO

4547. **Volumetric determination of cyanide by the use of cupric diethyldithiocarbamate as indicator.** Yoshimasa Tanaka and Setsu Yamamoto (Fac. of Pharm., Kumamoto Univ., Oe-cho, Kumamoto). *Japan Analyst*, 1960, **9** (1), 6–8.—Copper diethyldithiocarbamate (**I**) (10^{-4} M) in CCl_4 is decolorised when shaken with a trace of Hg^{2+} in an aq. phase. Cyanide (30 to 140 μg) is titrated with $Hg(NO_3)_2$ soln., with **I** in CCl_4 as indicator. The error is <1%. Halide ions and organic substances interfere with the titration, but CN^- can be separated by distillation from tartaric acid soln. (1%) in a current of air free from CO_2 within 15 min. K. SAITO

4548. **Complexometric micro-determination of silicic acid.** J. Jeník (Inst. Chem. Technol., Pardubice, Czechoslovakia). *Chem. Průmysl*, 1961, **11** (4), 188–190.—Silicic acid or alkaline silicates are pptd. with Co^{2+} as $CoSi_4O_9$ and the excess of the reagent is determined complexometrically. *Procedure*—To 10 ml of the sample (0·5 to 5 mg of Si) add $Co(NO_3)_2$ soln. (10%) (1 ml) and acetone (10 drops). Mix, and after 3 min. centrifuge for 3 min. Add acetone (5 g) and separate the supernatant liquid. Mix the residue with aq. methanol (1:4) (8 ml), centrifuge and repeat the procedure three times, adding acetone (5 drops) each time to decrease the surface tension. Dissolve the washed ppt. in a known vol. of 0·05M-EDTA (ammonium salt) (5 to 7 ml), and add aq. NH_3, buffer soln. (aq. NH_3 - NH_4Cl) (pH 8 to 10) and mixed indicator (Eriochrome black T and Tropaeolin OO), and titrate with 0·05M-$MgSO_4$ till the colour becomes bright red. J. ZÝKA

4549. **Direct spectrographic determination of rubidium, caesium, thallium and indium in silicates.** A. K. Rusanov, V. G. Khitrov and N. T. Batova. Publ.: Mineral Syr'e, Moscow, Vol. I, 1960, 310–315; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D51.—The method is based on the fractional evaporation of elements from the crater of a carbon electrode in the presence of potassium, thus reducing the size of the arc and weakening the cyanide lines and the spectra of undetermined elements. The sample, ground to −200 mesh, is mixed with an equal amount of K_2SO_4 and 40 mg of the mixture is placed in the carbon electrode. The analytical lines used are, Rb 4201 and 4215, Cs 4555 and 4593, Tl 3775, and In 4101 and 4511 A. The line Fe 4202 A is superimposed on the Rb line at Fe concn. of 5 to 10%; this is avoided by using the ISP-51 spectrograph and a UF-85 camera. The errors are ≯14%.

A. BURWOOD-SMITH

4550. **Organic reagents for inorganic analysis. Determination of germanium with gallein.** Peng-Joung Sun (Nat. Taiwan Univ., Formosa). *Formosan Sci.*, 1960, **14**, 81–88 (in English).—Treatment of slightly acid soln. of Ge with excess of alcoholic gallein (**I**) resulted in a red coloration followed by pptn. The red ppt., which was formed readily at pH 2 to 3, was insol. in most organic solvents, but slightl sol. in alcohols. For spectrophotometric study, cyclohexanol was added to the sample soln. of low pH to keep the complex in the colloidal state. Buffer soln. (10 ml) was added to a colloid of 10 μg of GeO_2 per ml, 14 ml of ethanol, 4 ml of cyclohexanol and 6 ml of 0·05% **I** soln. (in 95% ethanol). The pH of the resulting soln. was 0·8 to 1·8 units higher than that of the buffer soln. added. The absorption max. of the resulting soln. was at 510 mμ and did not change after 2 hr. when the pH was 5·6 to 6·4. When the sample soln. was buffered at pH 6, no pptn. occurred. As the reagent was unstable in H_2O, the presence of 40% by vol. of ethanol in the soln. was essential. More than 3 ml of 0·05% **I** soln. was needed to give constant extinction at 510 mμ when a mixture of 8 ml of GeO_2 soln. (10 μg of GeO_2 per ml), 20 ml of ethanol and 10 ml of buffer soln. (pH 4·6) (pH of the final mixture, 6) was used. The colour of the Ge-**I** complex in the soln. developed fully after 30 min. and its intensity did not change after 5 hr. The extinction of the coloured soln. determined at 510 mμ was linear up to 1·4 p.p.m. of Ge. In this method, a 110-fold excess of NaCl and a 4-fold excess of As did not interfere. The ratio of Ge to **I** in the chelate was determined as 1:2 at pH 6. The following procedure is recommended. Decompose a weighed sample with acid or fuse it with alkali and extract with hot H_2O and add enough $FeSO_4$ to destroy any oxidising agent. Add H_2O and conc. HCl to make the soln. 6N in HCl and distil. Collect the distillate in 20 ml of H_2O made 10N in HCl, and extract twice with

CCl_4. Extract the CCl_4 extract with H_2O, and neutralise and evaporate the aq. extract. Add 2 ml of buffer soln. (pH 4·6) to the residue and dilute with H_2O. Mix an aliquot, containing <70 μg of Ge, with 10 ml of the buffer and 20 ml of 0·01% alcoholic **I** and dilute to 50 ml with H_2O. Prepare a blank soln. without Ge. Measure the extinction of the soln. at 510 mμ after 1 hr., and determine the amount of Ge by reference to a calibration curve. CHEM. ABSTR.

4551. **Polarographic determination of germanium as catechol - germanic acid.** N. Konopik (Anorg. u. phys. Chem. Inst., Univ. Wien, Austria). *Monatsh. Chem.*, 1960, **91** (4), 717–728.—Germanium ($0·4 \times 10^{-4}$ to 7×10^{-3}M as GeO_2) gives a polarographic wave in a soln. M in $NaClO_4$ and 0·9M in catechol at pH 1·2, the height of which is proportional to the concn. of Ge. The half-wave potential becomes more negative with increase in the concn. of Ge (from −0·67 V *vs.* the S.C.E. at 0·461mM to −0·78 V at 7·30mM). With pure Ge soln., an aliquot (>2 ml) is mixed with basal soln. (>10 ml), and a weighed amount of catechol is added and dissolved. The pH is adjusted with $HClO_4$ or NaOH soln. (glass electrode) and the mixture is made up to 20 ml with $HClO_4$ soln. of the required pH. An aliquot is transferred to the apparatus previously described (Konopik and Werner, *Ibid.*, 1955, **86**, 937), O is removed with a stream of N and the polarogram is recorded with a satd. calomel reference electrode. The influence of pH, concn. of basal soln. and concn. of catechol on the wave-height and half-wave potential is discussed. In many cases, the Ge^{IV} is separated by distillation. The distillate is then received in 0·1M-glycine, the strongly acid distillate is adjusted, with cooling, to pH 1·5 with carbonate-free NaOH soln., a weighed amount of catechol is added, the pH is adjusted to 1·5, the vol. is made up with $HClO_4$ soln. of pH 1·5 and the polarogram is recorded. Under these conditions As^{III} gives a multiple wave which interferes with the Ge wave. This can be avoided by oxidising the As^{III} to As^{V} before distilling. Silicic acid does not interfere. R. E. E.

4552. **Spectroscopic detection of small amounts of hydrogen in germanium.** A. K. Babko and T. E. Get'man. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 36–47; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D85.—*Procedure*—Grind the germanium sample (1 g) and place a thin layer of the powder in a quartz or porcelain dish. Place the dish in a quartz tube (length 50 cm, diam. 20 mm) and heat to 950° to 1000°. Pass pure dry O through the tube for 1 hr. at the rate of 1·25 to 1·5 litres per min. and thence into a spectrographic cell consisting of a quartz tube (diam. 15 mm and length 180 mm) connected by a three-way tap to a rubber bulb for collecting emergent O and to an electrodeless gas discharge tube. The latter consists of two globes connected to one another by a capillary (diam. 2 mm). Cool the quartz tube with liquid air to freeze the steam passing through with the O. At the end of burning, evacuate the spectrographic cell to a pressure of 6×10^{-2} torr and cease cooling with liquid air. Photograph the spectra as the spectrographic cell warms up to room temp. and water vapour passes freely from the tube into the gas discharge tube. Register the lines H_α and H_β; the intensity of H_α is very small in comparison with the background.
K. R. COOK

4553. **Determination of tin by paper chromatography and by the use of a cellulose column.** S. Fişel, H. Franchevici and G. Balan (Inst. Chim. "Petru Poni," Acad. R.P.R., Iaşi). *Stud. Cercet. Ştiinţ. Chim., Iaşi*, 1960, **11** (1), 7–13.—*Paper method*—Best results are obtained by applying the test soln. (≡10 to 50 μg of Sn) in the form of a streak by means of an apparatus which synchronises the flow from the micro-pipette with the movement of the paper, and development, for 5 hr. by the ascending technique, with butanol satd. with N-HCl (**I**). The chromatographic streak thus formed is washed with an ethanolic soln. of diphenylcarbazone and dried. The intensity of the violet-coloured band is measured with an MGF colorimeter, with a sodium lamp and an automatic device to trace the curve on ultra-violet-sensitive paper. The results are not reproducible, and standards containing 10, 20 and 30 μg of Sn must be treated simultaneously. The error is ±4·5% in the presence of Cu. *Cellulose-column procedure*—A glass column (200 mm long, 15 mm in diam.) is made water-repellent with a thin film of silicone oil, then filled with 25 ml of **I**, and 4 g of powdered cellulose (S. & S. No. 123) is added. Excess of the solvent is allowed to run off, and the column is washed again with 10 ml of **I**. The test soln., containing a mixture of Sn and Cu (1% in 2N-HCl), is added, and when adsorption is complete the Sn is eluted with 25 ml of **I** in portions of 1 to 2 ml. Generally all the Sn is contained in the fraction between 5 and 20 ml. The last fraction is then tested for Sn by drying a drop of the soln. and treating it with a 1% ethanolic soln. of diphenylcarbazone. The Cu is completely eluted from the column with 30 ml of a mixture of butanol and conc. HCl (1 : 1). The Sn-containing eluate is evaporated to dryness on a water bath, the residue is dissolved in HCl and Sn is determined by titration with KIO_3. The error for the range of 0·2 to 2 mg of Sn in the presence of Cu is $>\pm 3·5\%$. H. SHER

4554. **Extraction of lead as tributylammonium iodoplumbate(II).** M. Ziegler (Anorg.-Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1961, **180** (5), 351–353 (in German).—Lead may be extracted from HCl soln. ($\simeq 1\%$) containing KI and tri-n-butylammonium chloride as tributylammonium iodoplumbate by dichloromethane. Separations may be made of Pb from Ca, Ba, Sr and metals of the sulphide group. T. R. ANDREW

4555. **Acid Chrome dark blue and Acid Chrome blue K as indicators in the EDTA determination of lead.** T. B. Styunkel' and Z. A. Mikhaleva. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 159–160; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D73.—It is shown that the sensitivities of Acid Chrome dark blue (C.I. Mordant Blue 7) and Acid Chrome blue K with respect to Pb^{2+} in alkaline tartrate soln. are $1·3 \times 10^{-5}$ and $1·3 \times 10^{-4}$ g-equiv. per litre, respectively, *i.e.*, they are greater than that of Chromogen black ET-00 (C.I. Mordant Black 11). In the determination of Pb in bronze or brass or lead electrolytes, ppt. of molybdate, sulphate, chromate or basic lead chloride are obtained and then dissolved by boiling in M-K Na tartrate (a few ml), 10% NaOH soln. (1 to 2 ml) and H_2O (100 ml). Ammoniacal buffer soln. (5 ml) is added to the hot soln. followed by indicator (6 to 7 drops) and the soln. is titrated with 0·05N-EDTA until the red-violet colour changes to blue. Interference from trace amounts of co-pptd. Cu is avoided by the

addition of 3% Na diethyldithiocarbamate soln. (2 to 3 drops). K. R. Cook

4556. **Titration of lead with EDTA in metallurgical samples with 1-(2-pyridylazo)-2-naphthol as indicator.** Masanori Hisada and Kaichi Kashikawa (Akenobe Mine, Mitsubishi Metal Mining Co., Asako-machi, Hyogo-ken). *Japan Analyst*, 1960, **9** (2), 87–91.—By the use of the Cu complex of 1-(2-pyridylazo)-2-naphthol in acetate buffer as indicator, the effect of Ca is eliminated, but Ba must be separated by pptn. of the Pb with H_2S. The standard deviation is less than by the use of Eriochrome black T as indicator. K. Saito

4557. **Determination of lead in sulphuric acid by square-wave polarography.** Yoshikazu Yasumori and Takao Nishimura (Yanagimoto Co., Kiya-machi, Nakagyo-ku, Kyoto). *Japan Analyst*, 1960, **9** (1), 37–41.—The peak potential of Pb shifts towards the negative region with increase in concn. of H_2SO_4 and overlaps that of H in >15M-H_2SO_4. The temp. coeff. is very large (3·6% per degree at 30°). The optimum concn. of H_2SO_4 is 10M and the temp. 40°. The wave height is proportional to the concn. of Pb at $<10^{-6}$M. The error is $\simeq 10\%$ for $<0{\cdot}1$ p.p.m. of Pb in industrial and reagent-grade sulphuric acid. K. Saito

4558. **Sampling errors in the X-ray fluorescence determination of titanium in a high-temperature alloy.** R. F. Stoops and K. H. McKee (Metallurgical Products Dept., General Electric Co., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 589–592.—The analysis by X-ray methods of ingots (8 in. square) of M252 alloy (Cr 19, Co 10, Mo 10, Ti 2·5, Fe 3, Al 1, C 0·15, Si 0·35%, with the balance Ni) gave results for Ti differing from those obtained by chemical analysis of bulk material. This was shown to be due to segregation of titanium in patterns dependent on grain structure. The problem has been overcome by casting a small test ingot, at the same time as the main ingot, of such a size that each of two X-ray examinations covers half the cross-sectional surface.

T. R. Andrew

4559. **Simultaneous polarographic determination of titanium and vanadium.** Soichiro Musha and Hiroya Takao (Fac. of Engng, Univ. Osaka Prefecture, Sakai, Osaka). *Japan Analyst*, 1960, **9** (3), 233–238.—Various supporting electrolytes were examined. In 0·1M-EDTA containing 0·02M-Na citrate of pH 6, the waves of Ti ($E_{\frac{1}{2}} = -0{\cdot}59$ V *vs.* the S.C.E.) and V ($-1{\cdot}3$ V) are both diffusion-controlled. The error of their simultaneous determination is $\pm 0{\cdot}3\%$ in the range 10^{-4} to 10^{-6}M. There is no interference from Al, Mn, Ca, Mg, Co or Ni; Fe and Cu must be removed by mercury-cathode electrolysis. K. Saito

4560. **Acid Chrome pure blue V as a reagent for titanium, zirconium, hafnium and thorium.** F. R. Sheyanova and V. I. Ganina. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1960, (1), 101–105; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D109.—At pH 2 to 5, Acid Chrome pure blue V (C.I. Mordant Blue 1) (**I**) forms predominantly violet complexes with Ti^{4+}, Zr, Hf and Th. Zirconium also reacts with **I** in 1N to 2N-HNO_3 with warming. The detectable minimum for each element is 2 to 2·5 μg per ml. The complexes contain the metal and **I** in the ratio 1:2. To determine Zr, to the acid soln. containing 2 to 10 μg of Zr as the nitrate (in a small flask) add 4 ml of buffer soln. of pH 5 and 0·2 ml of 0·05% aq. **I** soln., dilute to a known vol., mix, and measure the extinction with a green filter in a 2-cm cell. To determine Zr in magnesium alloys, dissolve the sample (20 to 30 mg) in HNO_3 (1:1), evaporate, add 0·001N-HNO_3 to 50 ml and measure the extinction. With a content of Zr of 0·3 to 0·5%, the relative errors are 2·1 to 5·9%. C. D. Kopkin

4561. **Determination of impurities in titanium and titanium dioxide.** A. G. Karabash, Sh.I. Pefzulaev, N. P. Sotnikova and S. K. Sazanova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 108–116; *Ref. Zhur., Khim.*, 1961, (4), Abstr. No. 4D108.—*Procedure*—Grind the titanium sample (0·25 g) and ignite for several hours in a platinum dish (until oxidation is complete) gradually raising the temp. to 1000°. Alternatively, dissolve the titanium in HCl, evaporate in the presence of HNO_3 and ignite for 30 min. at 600°. Mix the oxide with AgCl (4:1) in order to increase the intensity of the impurity lines. Place the ignited sample (60 mg) in the crater (diam. 4·3 mm, depth 8 mm) of a graphite electrode (anode) and photograph the spectra in a medium spectrograph. Construct calibration curves, correcting for background with the more sensitive lines. The sensitivity of the determination is 1×10^{-2} % for Zn, $\simeq 10^{-3}$ % for Na, Ca, Ba, Al, V, Cr, Mo, Fe, Co, In, Sn, Pb, Sb, Bi and Si, and $\simeq 10^{-4}$ % for Mg, Mn, Ni, Cu and Cd. Determine Na separately with a 5-amp. a.c. arc using the 5890-A line. Determine Si separately without mixing the sample with AgCl.

K. R. Cook

4562. **Analysis of some zirconium-base alloys.** S. V. Elinson, L. I. Pobedina and N. A. Mirzoyan. *Zhur. Anal. Khim.*, 1960, **15** (3), 334–338; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D183.—A method is developed for the determination of Al, Be, Mg, U and Zn in alloys based on Zr, after extraction of Zr with a $CHCl_3$ soln. of *N*-nitrosophenylhydroxylamine. *Procedure*—To 15 ml of 1·5N-H_2SO_4 add 5 ml of a 5% aq. soln. of cupferron (**I**) and 10 ml of $CHCl_3$, shake for 2 min., separate the org. phase and add it to the soln. of the sample, containing $\simeq 20$ mg of Zr, in N-H_2SO_4. After extracting the Zr, add to the aq. phase a second portion of the extractant, prepared from 15 ml of N-H_2SO_4, 1 ml of 5% **I** soln. and 10 ml of $CHCl_3$, repeat the extraction, and finally extract with 5 ml of $CHCl_3$. To extract 100 mg of Zr, use 20 ml of the 5% **I** soln. for the first extraction and up to 5 ml for the second. In the aq. phase, determine Al with aluminon, Mg with Titan yellow, Be with beryllon, U with H_2O_2, and Zn (in the absence of Mg) with EDTA (disodium salt). C. D. Kopkin

4563. **Separation of zirconium and hafnium in sulphuric acid solution by anion exchangers.** B. Trémillon, C. Cornet, M. Thibault and J. Huré (École de Phys. et de Chim., 10 rue Vauquelin, Paris, France). *Bull. Soc. Chim. France*, 1961, (2), 286–294.—The separation of Zr and Hf on Dowex-2 anion-exchange resin is investigated in soln. 0·7M with respect to H_2SO_4 and up to 2M with respect to total SO_4^{2-}. Elution of Zr and Hf from the column is effected with 2M-H_2SO_4 and Hf is displaced with a H_2SO_4 soln. of Zr^{IV}. Preparation of soln. of these elements free from colloids could only be effected by dissolving the cryst. $Zr(SO_4)_2.4\text{–}5H_2O$ in 0·1M to 4M-H_2SO_4 without heating. Analysis of the eluates

is carried out by gravimetric determination as oxide, volumetric determination with EDTA, spectrographic methods, and irradiation of mixtures of Hf and Zr with neutrons to produce ^{181}Hf which can be followed radiometrically. The behaviour of Hf and Zr on the resin is studied and the partition and elution coeff. for Zr and the elution coeff. for Hf at different concn. are determined. The change of partition coeff. with concn. shows that Zr forms a stable sharp front, and it is shown that the hafnium complex is less strongly held than the zirconium complex and is eluted in front of it. The max. ratio of the elution coeff. of the two elements (in 0·7M-H_2SO_4) is achieved with a total SO_4^{2-} concn. of 1·5M. A preparative separation of Zr and Hf is suggested in which a movable bed-column is used. When equilibrium is established, sulphate resin is fed in and Hf soln. is withdrawn at suitable rates at one end, and pure Zr soln. is fed in and Zr-containing resin withdrawn at the other. The rates are such that the Zr front remains at the centre of the column and the mixture of Zr and Hf to be separated is fed in at that point.

E. J. H. Birch

4564. **Separation of zirconium and uranium on anionite EDE-10P from sulphuric acid solutions.** M. N. Gordeeva and M. N. Myazdrikova. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 16–19; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D54.—The method is based on adsorption of the mixture on anionite EDE-10P (Cl^- form) followed by selective extraction of U with hydroxyammonium chloride. Neutralise the test soln. of the sulphates of Zr and U with aq. NH_3, add H_2SO_4 to a concn. of 0·2 to 0·3M, dilute to 50 ml and pass at a rate of 1 ml per min. through a column (diam. 1·3 cm and height 13 cm) of EDE-10P. Then wash the resin with N-hydroxylamine till U is completely extracted and elute the Zr remaining on the column with 3N-HCl. Determine Zr in the resulting soln. with EDTA (disodium salt) or photometrically with Alizarin red S, and U volumetrically or photometrically with H_2O_2. The method can be used to determine Zr and U in soln. containing Fe, Th, Ti and the rare-earth elements, part of which pass through into the percolate, the remainder being eluted with 0·25N-H_2SO_4, and also for the analysis of mixtures containing Zr 9·51, U 1·05, Th 5·4, rare-earth elements 6, Ti 9·5 and Fe 9·5 mg. The mean relative error of the determination is 7% for U and 3% for Zr.

C. D. Kopkin

4565. **Separations involving sulphides. II. Separation of platinum, gold, rhenium and quinquevalent antimony from zirconium.** G. B. S. Salaria (Gov. Coll., Dharmsala, Punjab, India). *Z. anal. Chem.*, 1961, **180** (5), 358–360 (in English).—Binary mixtures of Pt, Re, Au or Sb^V with Zr may be separated by the addition of 2N-Na_2S to an alkaline sample, decomposition of the thio-salt with HCl and separation of the sulphide by filtration; Zr remains in the filtrate.

T. R. Andrew

4566. **Photometric determination of minute amounts of magnesium in zirconium.** Tsugio Takeuchi, Hirotoshi Ito and Masami Suzuki (Fac. of Engng, Nagoya Univ., Chikusa-ku, Nagoya). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (6), 922–924.—Magnesium (<70 μg) is separated from Zr by passing an HF soln. of the sample through a column of cation-exchange resin, then eluted with NH_4Cl soln. and photometrically determined at 532 mμ with Titan yellow (C.I. Direct Yellow 9) in the presence of poly(vinyl alcohol). Interfering ions, including Mn and Ti, are co-pptd. with $Fe(OH)_3$; Ni is masked with CN^-.

K. Saito

4567. **Spectrographic determination of small amounts of various elements in zirconium oxide.** Tokunosuke Nakajima and Hiroyuki Fukushima (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Japan Analyst*, 1960, **9** (2), 81–86.—The use of AgCl (2%, w/w) as spectrographic buffer gives the best results. On excitation in a 15-amp. d.c. arc (arc gap 4·0 mm), vaporisation of impurities such as Co, Bi, Ni, Cr, V, Al, Mo, Mn, Zn and Fe is complete within 20 sec. Gallium is used as the internal standard.

K. Saito

4568. **Chromatographic separation of hafnium from zirconium and the determination of hafnium by isotope dilution.** G. M. Kolosova, Yüan-P'an Ch'êng and M. M. Senyavin. *Zhur. Anal. Khim.*, 1960, **15** (3), 364–366; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D31.—The method is based on the different stabilities of the sulphate complexes. The best separation is obtained by using 0·65N-H_2SO_4 for washing the cationite column. With 0·7N-H_2SO_4 the separation is significantly quicker, though not quant., but this does not interfere with the method of isotope dilution. For a complete analysis, the sample is dissolved by warming in HF - H_2SO_4, the soln. is evaporated and the residue is dissolved in conc. HCl. The hydroxides are pptd. from the soln., filtered off, washed with water and dissolved in 10 ml of 2N-HNO_3; a known amount of a soln. of ^{181}Hf in HNO_3 is added and the mixture is added to ≃1 g of KU-2KH12 resin. The resin is transferred to a column (10 mm diam.) containing 10 g of KU-2KH12, which is then washed with 0·7N-H_2SO_4 at a rate of 40 ml per hr.; an aliquot of the percolate is taken for radiometric analysis. The relative error is <1% of Hf in mixtures containing ≃10% of Hf, but higher if the Hf concn. is <3%. The method is used for the determination of Hf in eudialyte and zirconium and also in mixed oxides of Zr and Hf of various concn.

A. Burwood-Smith

4569. **Gravimetric determination of thorium using some carboxylic acids.** C. Bheemasankara Rao, P. Umapathi and V. Venkateswarlu (Andhra Univ., Waltair, India). *Anal. Chim. Acta*, 1961, **24** (4), 391 (in English).—At pH 2·6 to 3·4, Th can be determined by pptn. with 3,4-methylenedioxycinnamic, phenylpropionic and 3,4-methylenedioxyphenylpropionic acids and, at pH 3·8 to 4·2, *o*-methoxycinnamic, *o*-mercaptobenzoic and *o*-bromobenzoic acids can be used. The ppt. are ignited to ThO_2. *o*-Bromobenzoic acid is useful for the separation of Th from rare earths.

A. J. Bennett

4570. **Determination of metals with standard solutions of potassium ferrocyanide. XIII. Determination of thorium.** Yoshio Fujita (Fac. of Engng, Osaka Univ., Miyakojima-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 85–88.—Precipitation titration of Th (7 to 150 mg per 50 ml) with N-$K_4Fe(CN)_6$ is effected at pH 1·6 to 2·4 at 10° to 30°. Alizarin red S is the best indicator. The titration must be carried out slowly (2 drops per 5 sec.). Ions giving ppt. or reacting with $[Fe(CN)_6]^{4-}$ interfere.

K. Saito

4571. **Rapid determination of thorium with EDTA.** Shigeru Katsumata (Asahi Denka Ltd., Ogu, Arakawa-ku, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (11), 1933–1935.—Since tervalent rare-earth ions do not interfere with the EDTA titration of Th at pH 2 to 3 (catechol violet as indicator), the ppt. of Th and rare-earth oxalate is converted into hydroxide by boiling with NaOH soln. (30%) (50 ml) and dissolved in HCl (1:1) (10 ml). There would be significant interference from Fe^{III}, Cr, Al and phosphate, but these are separated by the oxalate pptn. K. SAITO

4572. **Amperometric titration of small amounts of thorium with EDTA.** P. N. Paleĭ and N. I. Udal'tsova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 299–305; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D39.—*Procedure*—Use two polarisable electrodes with anodic oxidation of EDTA at a platinum electrode at 0·4 to 0·5 V. Neutralise a soln. containing Th (0·3 to 15·0 mg) with aq. NH_3 to pH 2·0 to 3·5, charge the electrodes, stir the soln. for 3 to 5 sec., note the initial galvanometer reading, titrate with 0·1M-, 0·05M- or 0·005M-EDTA, stir the soln. for 3 to 5 min. after each addition of titrant, and note the current when the stirrer is switched on; Al, UO_2^{2+} and rare-earth elements (in 2-, 3- and 10-fold excess, respectively) do not interfere. The method is used to determine Th in monazite sand after separation of Th from rare-earth elements with oxalic acid. K. R. COOK

4573. **Organic azo dyes in quantitative analysis. III. Spectrophotometric determination of thorium.** M. R. Zaki and K. Shikar (Atomic Energy Estab., Cairo, Egypt). *Z. anal. Chem.*, 1961, **180** (3), 188–194 (in English).—Chrome Red Brown 5RD (C.I. Mordant Brown 41) forms a coloured complex with Th^{4+} (λ_{max} = 485 mμ, $E^{1\%}_{1cm} \simeq 800$). *Procedure*—Transfer 1 ml of soln. (containing 10 to 100 μg of Th^{4+} and 0·01N in HNO_3) to a 10-ml flask. Add acetate buffer (pH 4) (5 ml) and fresh 0·05% dye soln. (1·5 ml) and dilute to vol. Measure the extinction within 30 min.; Fe^{3+}, Zr^{4+}, SO_4^{2-} and Cl^- interfere seriously, U^{6+} and Ce^{4+} interfere only if their concn. exceeds that of the Th^{4+}, and Li, Na, K, Ni, Co, Cu^{2+}, Cd, Ca, Mg and Cr^{3+} are without effect. G. RUSSELL

4574. **Spectrophotometric determination of ammonia as indophenol.** W. T. Bolleter, C. J. Bushman and P. W. Tidwell (Monsanto Chemical Co., Texas City, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 592–594.—The several variables in the indophenol method have been studied and the following procedure is advocated. To a 50-ml flask add 25 ml of satd. H_3BO_3 soln containing 10 to 300 μg of NH_3, and, while swirling, aq. Cl (5 ml) followed by phenol soln. (8%) (5 ml). Heat in a steam bath for 3 min., then cool rapidly and add 3M-NaOH (5 ml); dilute to the mark, mix, and read the extinction at 625 mμ after 5 min. Under similar conditions, but with no aq. Cl, and 8·5 ml of NaOH soln. instead of 5 ml, *p*-substituted anilines also react with phenol to give blue colours. This test may be used to detect the *p*-isomer in the presence of the *o*- and *m*-isomers. T. R. ANDREW

4575. **The application of bromine chloride in analysis. Determination of hydroxylamine. Examination of the bromate - hydrochloric acid reaction.** K. Burger, F. Gaizer and E. Schulek (L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1961, **67** (4), 173–175.—The oxidation of hydroxylamine by BrCl, by elementary Cl, by bromate in HCl medium and by bromic acid in the presence of Hg^{2+} was investigated, and a method for the determination of hydroxylamine by BrCl oxidation is described. *Procedure*—A soln. containing 3 to 12 mg of hydroxyammonium chloride is measured into a bromine flask and a known amount of 0·1N-bromate - bromide reagent (2·7835 g of $KBrO_3$ plus 3·9670 g of KBr in 1 litre of H_2O) (at least twice the theoretical requirement) is added. The soln. is made up to 30 to 40 ml with H_2O followed by the addition of 5 to 10 ml of 20% HCl. After 5 min., 10 ml of fresh 5% KI soln. is added. The liberated iodine is titrated with 0·1N-$Na_2S_2O_3$ with starch as indicator (1 ml of 0·1N-BrCl ≡ 1·1583 mg of hydroxyammonium chloride). The method can also be used with 0·01N soln. for the determination of 0·3 to 1 mg of hydroxyammonium chloride. The error in both cases is ±0·5%. Examination of the reaction of bromate with HCl showed that, in the presence of excess of HCl, the formation of BrCl and elementary Cl takes place at a rapid rate; these are the active agents in the subsequent oxidation. B. VASZKO

4576. **Continuous determination of traces of nitric oxide.** C. Bokhoven and P. H. Tommassen (Dutch State Mines, Central Lab., Geleen, Netherlands). *Nature*, 1961, **190**, 435–436.—To determine traces (*e.g.*, 0·02 to 0·04 p.p.m.) of NO continuously in coke-oven gas or in polluted air, mix the sample with buta-1,3-diene (>0·05%) and irradiate for 5 sec. with u.v. light from a high-pressure mercury-vapour lamp. The NO is oxidised to NO_2. Absorb the NO_2 in Griess - Ilosvay reagent and measure the extinction by means of a flow-type colorimeter. The reactions appear to be stoicheiometric. A. R. ROGERS

4577. **Analysis of nitrogen dioxide, nitrosyl chloride and chlorine in gas mixtures.** F. Wolf and K. H. Schier (Inorg. Lab. Farbenfabrik Wolfen, Germany). *Z. Chem.*, 1960, **1**, 24–25.—The new method developed is based on H_2SO_4 absorption; this converts NOCl into $NO.HSO_4$, and NO_2 into HNO_3 and $NO.HSO_4$, while Cl remains unchanged. The apparatus consists of two absorbers containing 90% H_2SO_4, and one containing 10% KI soln. for Cl absorption. Total N is determined according to Lunge, N^{III} is measured by $KMnO_4$ titration, and iodine is titrated with $Na_2S_2O_3$. CHEM. ABSTR.

4578. **Reaction of 2-thiobarbituric acid with sodium nitrite.** N. S. Drozdov and V. P. Krylov. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (3), 476–479; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D154.—To develop a method for the photometric determination of NO_2^- or 2-thiobarbituric acid (**I**), the reaction of **I** with $NaNO_2$ has been studied in 0·001 to 0·01M soln. with excess of either reactant at various pH values. In both cases the appearance of the colour is due to the formation of Na 2-thioviolurate (max. absorption at 570 mμ). The intensity of the colour depends on the pH of the soln. (optimum 4·7 to 4·9). At lower pH values (3·8 to 4·5) the colour develops rapidly but then fades; at higher pH values (5·0 to 6·0) the colour develops slowly. An excess of $NaNO_2$ favours rapid loss of colour owing to oxidation. C. D. KOPKIN

4579. **Iodimetric determination of nitrate.** Tetsuro Murakami (Kogakuin, Tsunohazu, Shinjuku-ku, Tokyo). *Japan Analyst*, 1960, **9** (3), 248–250.—This determination was improved by heating the sample under reflux with KI (2 g for <20 mg of N) in 7N-HCl, in a current of Ar. The influence of NO is thus eliminated. The iodine condensed on the wall of the condenser is dissolved in KI and titrated by the usual method. Excess of H_2SO_4 also oxidises I^-, but the effect is eliminated by adding $MnCl_2$ (3 mg, for H_2SO_4 <5 times the equiv. of the HNO_3). K. SAITO

4580. **Polarographic determination of phosphate ions as bismuth phosphate.** Tsurumatsu Dono, Genkichi Nakagawa, Tsuyoshi Nomura and Minoru Aoki (Nagoya Inst. Tech., Gokiso-cho, Showa-ku, Nagoya). *Japan Analyst*, 1960, **9** (2), 96–99.—Phosphate (>0·1 millimole) is pptd. with Bi^{3+} (5 to 10 times the theoretical amount) in 0·5N to 0·9N-$HClO_4$, filtered off, washed with 0·6N-$HClO_4$, and dissolved in 6N-HNO_3 (20 ml). For quant. pptn., the concn. of NO_3^- must be <M. The soln. is diluted with 4M-$NaNO_3$ (10 ml) and gelatin soln. (0·1%, 5 ml) to 100 ml and the Bi determined polarographically. Sulphate is removed with $Ba(NO_3)_2$, but co-pptn. occurs with >100 mg of SO_4^{2-}. Tin and Sb give ppt. under the same conditions and must be removed by electrolysis in HCl soln.; As is removed by heating with $HBrO_3$ and $HClO_4$. There is no interference from Fe (<150 mg per 100 ml), Cu, Pb, Mn, Co, Zn, Ni, Al, alkaline-earth and alkali metals, but Cr and W must be absent. K. SAITO

4581. **Gas-chromatographic analysis of some volatile phosphorus compounds.** S. H. Shipotofsky and H. C. Moser (Dept. of Chem., Kansas State Univ. of Agric. and Appl. Sci., Manhattan, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 521–523.—The method described is rapid and accurate. Mixtures of phosphorus trichloride and thiophosphoryl chloride and of phosphorus trichloride and phosphoryl chloride are separated on a 246-cm column of 10% Kel-F 90 on Fluoropak 80 at 103° and 72°, respectively. Mixtures of dimethyl phosphite and diethyl phosphite are separated on an 86-cm column of 12·2% di-n-butyl phthalate on Fluoropak 80 at 107°. A simple dependable thermal-conductivity detector is used, made from borosilicate glass with tantalum filaments. The area per cent. of each peak agreed closely with the weight per cent. of the corresponding component of the mixture. C. B. BAINES

4582. **Separation and determination of arsenic. Application to the determination of arsenic in the zinc and lead industry.** N. Dreulle. *Chim. Anal.*, 1961, **43** (4), 165–168.—*Procedure for zinc and lead minerals*—Treat the sample (2 g for up to 0·1% of As, or 0·2 g for 0·1 to 1·5% of As) with 20 ml of HCl and 10 ml of HNO_3 and, when the reaction is complete, add 20 ml of 50% H_2SO_4 and evaporate to fumes. Dissolve the residue in 50 ml of H_2O and boil. Add 10 ml of an aq. soln. containing 5% of KI and 5% of $Na_2S_2O_3$, cool and adjust the vol. to 100 ml with H_2O. Extract a 25-ml aliquot with 20 ml of 0·5% K ethylxanthate (**I**) soln. in CCl_4 for 1 min. Extract the aq. layer with a further 10 ml of **I** soln. Combine the CCl_4 extracts and shake with 25 ml of bromine water. Allow to separate and discard the CCl_4. Filter the aq. layer, dilute it to ≃70 ml, and heat to 95° to expel the excess of Br, then boil for 2 min. Add 5 ml of 1% ammonium molybdate soln. in 5N-H_2SO_4 and 5 ml of 0·15% hydrazine sulphate soln., and boil for 5 min. Cool, dilute to 100 ml with H_2O, and read the extinction at 635 mμ. Refer the result to a standard curve. *Procedure for lead and zinc metals*—Dissolve the sample in HNO_3 (1:1) and proceed as described above. Tin, Cu and Sb do not interfere; results for known amounts of added As were accurate to ±3%. R. A. HENDEY

4583. **Extraction of arsenic(V) from sulphuric acid - potassium bromide solutions and its analytical use.** K. Študlar (V. I. Lenin Works, Res. and Test Inst., Plzeň, Czechoslovakia). *Talanta*, 1961, **8** (4), 272–273 (in English).—Quinquevalent As (100 μg) can be quant. extracted from 25 ml of H_2SO_4 soln. (14 to 17N) containing <200 mg of KBr with CCl_4. G. S. ROBERTS

4584. **Chelatometric determination of arsenic acid as zinc ammonium arsenate.** Chung Hyen Sub (Nat. Univ., Pusan, Korea). *J. Pharm. Soc. Korea*, 1960, **5** (1), 16–19.—Determination of arsenic acid by pptn. as $ZnNH_4AsO_4$ (**I**) and titration of Zn in the ppt. with EDTA has been investigated. **I** was sol. in NH_4Cl - aq.NH_3 buffer soln. of pH 10, and back-titration was unnecessary as in the case of $MgNH_4AsO_4$. The end-point was clear, whether AsO_4^{3-} were present or not. This method is simpler and more rapid than the gravimetric method. The error is ±0·3%. CHEM. ABSTR.

4585. **Separation of arsenic, antimony and tin by means of anionites.** M. N. Zvereva and E. A. Dmitrieva. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 41–45; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D56.—The method is based on adsorption of the elements on the anionites EDE-10P or AV-16, with their subsequent elution. EDE-10P is the more convenient resin, since it requires smaller vol. of eluents. Pass 50 ml of the soln., containing As^{III}, Sb^{III} and Sn^{IV} and 5 moles of HCl per litre, through 10 g of EDE-10P previously treated with 5N-HCl. Elute the As with 150 ml of 5N-HCl, the Sn with 250 ml of 0·5N-HCl, and the Sb with 300 ml of 5N-H_2SO_4. In the resulting eluates determine As and Sb by the bromate method, and Sn gravimetrically (small amounts of As are determined photometrically as the molybdoarsenic heteropoly-acid). The method gives a quant. separation with ratios of As:Sb:Sn of 1:1:1 and 1:100:100, and is used for the analysis of bronze and synthetic soln. of a corresponding composition. In this case most of the Cu is eluted with 150 ml of 5N-HCl, the remaining Cu and Sn with 150 ml of 2N-HCl, Zn with 100 ml of 0·5N-HCl, Pb with 200 ml of hot water, and Sb with 200 ml of 5N-H_2SO_4. This method gives somewhat higher contents of Pb and Zn in bronze than does the Government standard method; this is due to the absence of losses of the elements during their separation. C. D. KOPKIN

4586. **Detection of arsenic, antimony and tin in forensic toxicology by paper chromatography.** Swarup Narain Tewari (18/3A The Mall, Kanpur, India). *Z. anal. Chem.*, 1961, **180** (2), 109–110 (in English).—The tissue (30 to 40 g of liver or 20 to 30 g of bone) is wet-oxidised with HNO_3 (50 ml) and H_2SO_4 (10 ml). After removal of acid by evaporation, the residue is dissolved in H_2O (1 to 5 ml) and 10 to 20-μl aliquots are chromatographed by the ascending technique on Whatman No. 1

paper for 6 hr. with the organic phase of butanol - 3N-HCl. Spots are revealed by spraying with 0·5% dithizone soln. in $CHCl_3$. R_F values are 0·83 (As), 0·34 (Sb) and 0·99 (Sn), and 2 μg may be detected. G. RUSSELL

4587. **Determination of antimony(III) and free hydrochloric acid in mixtures.** S. S. M. A. Khorasani (Dacca Univ., Dacca-2, East Pakistan). *Anal. Chim. Acta*, 1961, **24** (4), 316–318 (in English). —The mixture of $SbCl_3$ and HCl is titrated with 0·1N-alkali in the presence of phenolphthalein, the titration being completed in a boiling soln. After the titration, solid K H tartrate is added and the soln. is boiled until the pptd. Sb_2O_3 is completely dissolved. The soln. is then cooled, made sufficiently alkaline with $NaHCO_3$ and titrated with 0·1N-iodine. This gives the amount of Sb^{3+}, and the free HCl originally present can be calculated. An accuracy of ±1·0% for both Sb^{3+} and HCl can be obtained. A. J. BENNETT

4588. **Detection of antimony in copper alloys by surface treatment.** R. F. Khovyakova and S. A. Lomonosov. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 142–145; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D161.—The method is based on the colour reaction between methyl violet and $SbCl_6^-$. *Procedure*—Carefully clean a cavity in the surface of the sample with dil. HNO_3, wash with water and dry with filter-paper. Place two drops of HNO_3 (1:1) on the clean surface. After the reaction has subsided, transfer the soln. and ppt. to a 10-ml cylinder, and wash the whole 5 or 6 times with water and with 2 or 3 drops of HCl (1:1). Dilute the soln. in the cylinder to 1 ml, add 1·5 ml of concn. HCl, then 10% $SnCl_2$ soln. dropwise till the green colour of the soln. is discharged and 1 or 2 drops in excess; add 10% $NaNO_2$ soln. till the green colour returns and 1 or 2 drops in excess, set aside for 3 to 5 min. and add satd. urea soln. dropwise till foaming ceases; dilute to 8 ml, add 2 or 3 drops of 0·2% methyl violet soln., stir with a stream of air, add 0·5 ml of toluene and shake for 10 to 15 sec. In the presence of Sb the org. layer is coloured blue with a violet tinge. With very small amounts of Sb the colour is pale blue. As a confirmatory reaction, shake part of the extract with the $SnCl_2$ soln.; the Sb^V is reduced and the org. layer is decolorised. The method can be used to detect 0·009 to 7% of Sb in copper alloys. The procedure takes 30 to 40 min.

C. D. KOPKIN

4589. **Chromatography of quadrivalent protactinium in hydrochloric acid medium on anion-exchange resins.** E. Pluchet and R. Muxart (Inst. de Radium, Lab. d'Arcueil, 4 Ave. de la Convention, Paris, France). *Bull. Soc. Chim. France*, 1961, (2), 372–373.—The behaviour of Pa^{IV}, Pa^V, Th^{IV} and U^{IV} on anion-exchange resins is compared. It is shown on the tracer scale that Pa^V reduced to Pa^{IV} by Cr^{2+} in an atmosphere of H by the method of Bouissières and Haissinsky (*J. Chem. Soc.*, 1949, S257) is not retained by anion-exchange columns of Dowex 1 or Amberlite IR-401 in 6N to 12·6N-HCl, but Pa^V is retained and can be eluted with 6N to 7N-HCl that is 0·1N with respect to HF. Quadrivalent Th is eluted with conc. HCl, but U^{IV} is retained. As Zr^{IV} is retained at HCl concn. >9N it is suggested that separation of Zr and Pa can be improved by a preliminary reduction of the Pa. The reduction of Pa^V to Pa^{IV} by Cr^{2+} is shown to be at least 95%.

E. J. H. BIRCH

4590. **Extraction of bismuth as iodide with isoamyl acetate and isoamyl alcohol.** H. A. Mottola and E. B. Sandell (School of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (4), 301–306 (in English).—Bismuth is extractable both as BiI_3 and $HBiI_4$ according to the solvent and iodide concn. Extraction as BiI_3 is preferred, as a number of metals are extractable as iodo-acids. Aq. soln. (20 ml) containing 5×10^{-4}M-$BiSO_4$, H_2SO_4 and KI were shaken at 25° to 30° for 10 min. with organic solvents (5 ml), and the amounts of Bi extracted were determined. With isoamyl acetate as solvent the optimum KI concn. was 0·0065M, indicating that the Bi is extracted mainly as BiI_3. At this concn. the extraction coefficient ([Bi] isoamyl acetate/[Bi] water) is approx. 130. Increase of extraction with increasing H_2SO_4 concn. from 1N to 5N is due to repression of hydrolysis and to salting out of BiI_3. Isoamyl alcohol extracts $HBiI_4$ as well as BiI_3, the extractability remaining constant from 0·015M to >0·10M-KI. At concn. of KI <0·02M, mixtures of isoamyl alcohol and isoamyl acetate extract BiI_3 better than either alone. Under the optimum conditions for extraction of Bi, some Hg^{2+}, Sb^{3+} and Pb^{2+} are also extracted.

A. J. BENNETT

4591. **Spectrographic determination of impurities in metallic bismuth.** I. G. Yudelevich and V. G. Kovaleva. *Sb. Trud. Vses. Nauch.-Issled. Gorn.-Metallurg. Inst. Tsvet. Met.*, 1959, (5), 202–205; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D149.—A procedure is developed for the spectrographic determination in bismuth of Pb 0·1 to 6, Cu 0·001 to 0·04, Ag 0·02 to 0·5, Sb 0·02 to 1·0, Te 0·001 to 1·0, As 0·001 to 0·1, and Zn and Cd 0·001 to 0·05%. In analysis for Pb, Ag, Cu and Sb, the spectra are excited in a spark discharge between cast cylindrical samples of diam. 9 mm. In the determination of Zn, Te, As and Cd, powdered samples are evaporated from a groove in a carbon electrode in an a.c. arc at 11 amp. With spark excitation, the spectra are photographed for 50 sec. with lens-less illumination of the slit, and with arc excitation with replacement of the lower electrode, for 2 to 50 sec. The lines used are given. The initial standard is prepared synthetically, and the others by dilution with pure bismuth. The error of the determination is 10%. The method is used during the refining of bismuth and for standardisation. C. D. KOPKIN

4592. **Separation of vanadium and phosphate ion by means of anionites.** Yu. V. Morachevskiĭ and M. N. Gordeeva. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 10–15; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D55.—The method is based on the selective adsorption of PO_4^{3-} from HCl or H_2SO_4 soln. by the anionite EDE-10P or PE-9 (Cl^- form), oxidation of the V^{IV} in the percolate to V^V, and titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$. *Procedure*—To the test soln. add HCl or H_2SO_4 to a concn. of 0·1N and ^{32}P (as $NH_4H_2PO_4$) as radioactive indicator, and pass SO_2 for 5 min. to reduce V^V to V^{IV}, which is not adsorbed by the anionite. Boil the soln. till no more SO_2 is liberated, then cool the soln. and pass it at a rate of 1 ml per min. through a column of diam. 1 cm containing a 15 to 18-cm layer of EDE-10P or PE-9. Wash the resin with water at a rate of 2 to 5 ml per min., and determine V in the percolate after oxidising it to V^V. Elute PO_4^{3-} from the resin with 100 ml of 2N-HCl and determine P radiometrically in an aliquot of the eluate. The relative errors in the determination of PO_4^{3-} and V are 2 and 4%, respectively. The method can be

used to separate 0·82 to 21·5 mg of V from 0·106 to 42·4 mg of P, and also for the separation of V plus Ca from PO_4^{3-} in HCl soln. Iron and PO_4^{3-} cannot be separated in this way, because of the formation of complex phosphates. C. D. KOPKIN

4593. **Application of EDTA for the chromatographic separation of vanadium(V) and chromium(III).** D. Šiškov. *Himija i Ind.*, 1960, **32** (3), 69–71.—A method is developed for quant. chromatographic separation of V from Cr in ratios of 10^4:1 and 1:10^4, making use of EDTA as the complex-forming agent. An anion exchanger EDE-10P (Cl^- form) and a cation exchanger KY-2 (Na^+ form) are used in bead size of 0·5 to 1 mm. A 50-ml burette (diam. 10 mm) is filled with 10 g of resin. The rate of flow is 3 ml per min. The separation is carried out in weakly acid medium (pH between 3 and 5) in the presence of 50 ml of 0·5% EDTA (disodium salt) soln. At these pH values, V forms a negatively charged complex which is retained by the anion exchanger but passes into the percolate when a cation exchanger is used. Under the same conditions, Cr remains positively charged and is retained by the cation exchanger, but passes into the percolate when an anion exchanger is used. Chromium is eluted from the cation exchanger with 4N-HCl.

ABSTR. BULG. SCI. LIT.

4594. **Determination of vanadium in tungsten-vanadium alloys.** E. Lassner and R. Scharf. (Metallwerk Plansee, A.-G., Reutte, Tirol). *Planseeber. Pulvermet.*, 1961, **9** (1–2), 51–53 (in German).—In the presence of tartaric acid, W does not interfere in the determination of V by the procedure of Flaschka and Abdine (*Anal. Abstr.*, 1957, **4**, 361). This has been applied to the determination of V (>2%) in V - W alloys (0·5 g). For smaller amounts of V it has been found that tartaric acid also eliminates interference by W in the photometric method with 1,2-di-(2-aminoethoxy)ethane-*NN'*-tetra-acetic acid, according to Martinez and Castro (*Anal. Abstr.*, 1959, **6**, 2962). T. R. ANDREW

4595. **The precipitation of niobium oxinate of definite composition.** L. Kosta and M. Dular (Nuclear Inst. "Jozef Stefan," Ljubljana, Yugoslavia). *Talanta*, 1961, **8** (4), 265–269 (in English).—Crystalline niobium 8-hydroxyquinolinate [$NbO(C_9H_6ON)_3$] can be obtained by adding five times the theoretical amount of urea to a soln. of Nb in hot M-oxalic acid (100 ml) containing conc. H_2SO_4 (10 ml) and a 50% excess of 8-hydroxyquinoline. By this method >99% of the Nb in the sample can be recovered, provided that the pptn. is carried out with a freshly prepared soln. of Nb. Data on the u.v. and i.r. spectra, electron diffraction, solubility in org. solvents and thermolysis of the compound are presented. G. S. ROBERTS

4596. **Separation of niobium, tantalum and titanium on anion-exchange resin.** S. M. Chernobrov and N. P. Kolonina. Publ.: "Khromatografiya, ee Teoriya i Primenenie," Akad. Nauk SSSR, Moscow, 1960, 214–217; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D40.—The method is based on the adsorption of Nb, Ta and Ti by an anion-exchange resin (EDE-10 or EDE-10P) (Cl^- form) from HF soln. and their subsequent elution with acid. *Procedure*—Dissolve the test sample in HF and pass the soln. through a column (diam. 3 cm) containing the resin (300 g) (height of layer 130 cm). Elute first the Fe and then the Nb with M-HCl plus 0·05M-HF at a rate of 2 ml per sq. cm per min. About 90% of the Nb is eluted free from Ta and Ti. Elute the Ti, together with the remaining Nb and 5 to 7% of the Ta, with 3M-HCl. Elute the remaining Ta with 5M to 6M-HCl plus 0·5M-HF; the eluted Ta is free from Ti and Nb. The method has been used to separate components of a technical hydroxide containing Nb_2O_5 68·65, Ta_2O_5 2·95, TiO_2 1·4, and Fe_2O_3 3·5%; the separated Nb_2O_5 contained <0·002% of TiO_2 and <0·05% of Ta_2O_5. K. R. COOK

4597. **Colorimetric determination of tantalum and niobium with methyl violet.** A. T. Pilipenko and V. A. Obolonchik. *Vopr. Poroshk. Metallurg. i Prochnosti Mater., Akad. Nauk UkrSSR*, 1960, **8**, 131–136; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D90.—It is shown that the reaction product of a tantalum fluoride complex with methyl violet (**I**) can be extracted with toluene, and that under the optimum extraction conditions for Ta (pH 1·9 to 2·3) the fluoride complex of Nb does not react with **I**. The optimum concn. of F^- and **I** for obtaining a combination of Ta with **I** are 5 mg per ml and 0·02%, respectively. Toluene soln. of this compound have three absorption maxima, at 330 mμ (mol. extinction coeff. 150,000), 550 mμ (22,700) and 600 mμ (30,900). The coloured soln. are stable for 2 hr. and Beer's law is obeyed at concn. up to 60 mg of Ta per ml; Nb does not interfere. **I** can be used for the determination of from 0·02 to 1·5% of Ta in niobium metal and in niobium pentoxide; Ti and Zr do not interfere, but NO_3^- and ClO_4^- do. A. BURWOOD-SMITH

4598. **X-ray determination of the products of chemical reaction during the spectrographic determination of tantalum.** N. I. Tarasevich, K. A. Semenenko and K. N. Semenenko. *Vestn. Moskov. Univ., Ser. Khim.*, 1960, No. 3, 37–39.—The reaction products of Ta_2O_5 with C, Ta_2O_5 with SiO_2 and C, and Ta_2O_5 with Si and C in the crater of a carbon electrode during spectrographic analysis show that Ta_2O_5 is best reduced in the presence of free Si. The lower oxide (TaO) is then formed.

A. BURWOOD-SMITH

4599. **Sulphur and sulphur chloride methods for the determination of oxygen in metals and oxides.** K. E. Kleiner. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 150–157; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D132.—The applicability of the sulphur method (*Ref. Zhur., Khim.*, 1956, Abstr. No. 78,488) and the sulphur chloride method (*Anal. Abstr.*, 1958, **5**, 471) for the determination of O in various metals and alloys was studied. It is shown that the sulphur method can be used in the analysis of most metals, except for samples containing oxides of Al, Mg, Be, Ti and Zr; >0·01% of O can be determined in an atmosphere of N (in 20 to 40 min.), and $>10^{-4}$ % of O by wt. in a low vacuum (in ≃6 hr.). The sulphur chloride method can be used for determining >0·01% of O in any metal, oxide or salt, and takes from 15 min. to 4 hr. according to the sample. C. D. KOPKIN

4600. **Spectrographic determination of impurities in high-purity sulphur.** N. K. Rudnevskiĭ and O. P. Malkova. *Trudy Khim. i Khim. Tekhnol. [Gor'kiĭ]*, 1960, (2), 367–368; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D189.—Mix 4 g of the sample with 20 mg of carbon powder in a quartz dish, burn off the S, and place the carbon powder in a cavity in a graphite electrode. Excite the spectrum

in a d.c. arc at 10 amp. Construct calibration curves from the lines Ni 3050·8, Co 3412·6, Ag 3280·7, Cu 3274, Cr 4254·3 and Mn 2801·1 A. For comparison, the background near the analytical lines is sometimes used. The position of the curves depends on the mol. composition of the standards, so that, to reproduce the same conditions, the metal sulphides are added to the standards. The sensitivity is 10^{-5} to 10^{-6} %. The proportion of the elements lost during the ignition is constant.

C. D. KOPKIN

4601. **Spectrographic determination of total carbon in elementary sulphur.** B. M. Maslennikov and L. V. Romanova. USSR Pat. 136,592 (14.3.1961). —Aluminium electrodes are used, and C is determined from the line at 2478·57 A excited in a low-voltage spark. The sample is ignited at 5 amp. The background near the line is used for comparison, and the content of C found from a calibration curve. The mean relative error of the determination is 5%.

C. D. KOPKIN

4602. **Separation of selenium from sulphur.** M. I. Erdenbaeva and N. A. Dragavtseva. *Izv. Akad. Nauk KazSSR, Ser. Khim.*, 1960, [1(17)], 59–62; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D57.—When S and Se are heated with KCN at 200° for 15 to 30 min. (longer heating and higher temp. cause loss of S and Se) they are quantitatively converted into KSCN and KSeCN. Treatment of the melt with HCl (1:2) dissolves KSCN, but decomposes KSeCN with the pptn. of Se (red form). The presence of KSCN does not affect the complete decomposition of the KSeCN; the yield of Se is ≃98·8%. This is the basis of a method for the separation of S and Se, which is recommended for the analysis of sublimates obtained in the treatment of slimes from the electrolytic refining of Cu with elemental S, and also for the rational analysis of selenium compounds in slimes and dusts of metallurgical origin.

C. D. KOPKIN

4603. **Determination of sulphate ions with EDTA. III. Determination of phosphate and sulphate ions as magnesium ammonium phosphate and lead sulphate.** Nobuhiko Iritani and Tomoo Tanaka (Shizuoka College of Pharmacy, Oshika, Shizuoka). *Japan Analyst*, 1960, **9** (1), 1–5.—The effect of nitrate, used for the preparation of magnesia mixture, on the determination of SO_4^{2-} in the filtrate from $MgNH_4PO_4.6H_2O$ was studied. Precipitation of >0·2 mg of PO_4^{3-} per ml is satisfactory in the presence of >20 times its wt. of NH_4NO_3 and >1·5 times the equiv. of Mg^{2+}. The pptd. phosphate is dissolved in HCl, neutralised and titrated with EDTA (disodium salt) in the usual way. The sulphate (>1 mg) in the filtrate is pptd. with a known amount of $Pb(NO_3)_2$ at pH 3 to 4 in 25% ethanol, and the excess of Pb^{2+} is titrated in acetate buffer of pH 5·0 to 5·5 with EDTA (disodium salt) to xylenol orange.

K. SAITO

4604. **Iodimetric determination of persulphate in sulphuric acid solution.** Y. Kishore Gupta (D.S.B. Govt. Coll., Nainital, India). *Z. anal. Chem.*, 1961, **180** (4), 260–265 (in English).—The conditions affecting the iodimetric determination of $S_2O_8^{2-}$ have been studied, and optimum conditions are given. *Procedure*—To 25 ml of H_2O add 15 ml of conc. H_2SO_4; then immediately add 10 ml of $S_2O_8^{2-}$ soln. (0·01 to 0·2N), set aside for 5 min., add 100 ml of H_2O and 10 to 15 ml of 10% KI soln. and titrate the liberated iodine with $Na_2S_2O_3$ soln. (0·01 to 0·2N). Results are accurate to within ±0·3%.

T. R. ANDREW

4605. **Colorimetry of sulphur anions. III. Determination and evaluation of polythionates above trithionate.** P. J. Urban (Govt. Metallurg. Lab., Witwatersrand Univ., Milner Park, Johannesburg, S. Africa). *Z. anal. Chem.*, 1961, **180** (2), 110–116 (in English).—The previously described procedure (*Anal. Abstr.*, 1961, **8**, 4149) for polythionates (reaction with CN^- and colorimetric measurement of the SCN^- produced) has been applied to the determination of the concn. of $S_nO_6^{2-}$ in soln. and of the value of *n*. Direct reaction of $S_nO_6^{2-}$ with CN^- produces (*n* − 3) equiv. of SCN^- and 1 equiv. of $S_2O_3^{2-}$. The latter will produce further SCN^- in the presence of a $CuCl_2$ catalyst. The calculations are based on these two amounts of SCN^-. Results with soln. of compounds with *n* = 4, 5 or 6 are compared with those by an iodimetric method. Agreement within 3% is obtained.

IV. Colorimetric evaluation of sulphur sols. P. J. Urban. *Ibid.*, 1961, **180** (2), 116–119 (in English).—The sulphur sols, considered as polythionates, $S_nO_6^{2-}$, in which *n* = 15 to 140, are also studied by the cyanolysis procedure. Under the given conditions, S reacts with CN^- to form SCN^-. The accuracy in this case is limited by the fact that the value of *n* depends on the small difference between two large amounts of SCN^-. A sulphur sol prepared by the method of Bassett and Durrant (*J. Chem. Soc.*, 1939, 2919) and aged for 3 days was found to have a value of *n* of ≃ 16.

G. RUSSELL

4606. **Radioactivation analysis by the use of short-lived nuclides. III. Determination of selenium in sulphur and sulphur compounds.** Toshio Nakai, Seishi Yajima, Minoru Okada, Koreyuki Shiba and Terutomi Maki (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 107–109.—When Se (>0·1 p.p.m.) in sulphur compounds is determined by the use of ^{77m}Se with a well-type NaI scintillator, the influence of ^{77m}Ge is eliminated by measuring the spectrum twice, at a 20-sec. interval. Nuclides giving γ-rays of similar energies have longer half-lives than 1 min. The variation is ≃10% for several μg of Se.

K. SAITO

4607. **Determination of a trace of mercury in metallic selenium with dithizone.** Satoru Uehara and Shuichi Hamada (Tokyo Coll. of Sci., Kagurazaka, Shinjuku-ku, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (9), 1580–1583.—Irving's reversion method (*J. Chem. Soc.*, 1949, 537) was applied to the determination of Hg (<20 p.p.m.) in selenium for semi-conductors. *Procedure*—Heat the powdered sample (5 g) with HNO_3 (15 ml), dilute, add 2M-Na acetate (washed with dithizone in $CHCl_3$) (10 ml), adjust to pH 5 with aq. NH_3 and make up to 250 ml. Add an equal vol. of M-ammonium sulphamate to a 10 to 30-ml portion, adjust the pH to 5·0 to 5·5 and shake with dithizone in $CHCl_3$ (1·2 mg per 100 ml) (20 ml) for 1 min. Wash the $CHCl_3$ layer with NaCl soln. (10% in 0·015N-HCl) (20 ml). Shake a portion of the org. layer with the reversion mixture (10·2 g of K H phthalate and 30 g of KI in 500 ml of water containing a trace of $Na_2S_2O_3$), and measure the extinction at 600 mμ.

K. SAITO

4608. **Derivatives of trihydroxyfluorone as reagents for tellurium.** G. G. Shitareva and V. A. Nazarenko.

Ukr. Khim. Zhur., 1960, **26** (3), 368–372; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D108.—Fifteen derivatives of 2,6,7-trihydroxy-3-fluorone substituted in position 9 were studied as reagents for Te^{4+}. The most satisfactory were the propyl and 2-hydroxy-1-naphthyl derivatives. K. R. COOK

4609. **Determination of polonium-210 in effluent treatment plant solutions.** U.K.A.E.A. (Production Group, Technical Branch, Windscale, Cumberland, England). U.K.A.E.A. Report PG 207(W), 1961. 6 pp.—Full experimental details are given. To a soln., containing <10 disintegrations per min. of ^{210}Po, are added $MnSO_4$ and $KMnO_4$ and the Po is co-pptd. with MnO_2, which, after being washed with 2M-HNO_3 and H_2O_2, is α-counted.
G. J. HUNTER

4610. **Determination of small amounts of molybdenum.** V. A. Khalizova, L. P. Volkova and E. P. Smirnova. Publ.: "Mineral. Syr'e," Moscow, 1960, (1), 307–309; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D101.—A method is described for the separation of Mo from accompanying elements (Fe, Cu, V, Cr, Bi and W) in the analysis of complex mineral raw materials (*e.g.*, sulphide ores and granite). The Mo is determined polarographically. Heat 1 to 2 g of sample with 10 ml of HCl (1:1) to boiling, add 2 ml of HNO_3 and evaporate to dryness. To the residue add 10 ml of 6N-H_2SO_4, fume off the H_2SO_4, boil with water in the presence of a few drops of H_2SO_4, add 1 g of citric acid, dilute to 50 ml (with a content of Cr and V of $>0{\cdot}1\%$, add 200 ml of Na_2SO_3), filter, and pass the soln. through cationite KKh-2, discarding the first 20 ml of percolate. Evaporate an aliquot of the resulting soln., and decompose the citric acid with a mixture of H_2SO_4 and HNO_3. Dissolve the dry residue in M-$HClO_4$ and 0·7M-H_2SO_4 and, after de-aeration, polarograph at $+0{\cdot}2$ to $-0{\cdot}6$ V. With a content of 0·001% of Mo, the mean deviation is $\pm 13\%$.
C. D. KOPKIN

4611. **Indirect complexometric determination of molybdate as lead molybdate.** Masuo Umeda (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 172–175.—Lead molybdate is pptd. in an acetic acid soln. in the presence of a known excess of Pb^{2+}. The supernatant liquid is treated with KCN soln. (5%) (2 ml), $NH_4F.HF$ soln. (50%) (2 ml) and triethanolamine soln. (50%) (2 ml), then adjusted to pH 9 to 10 with aq. NH_3 and titrated with 0·02M-EDTA (to catechol violet). There is no interference from Cu, Fe^{III}, Co, Ni, Zn, Ca, Mg, Ba, Ag or Hg, but SO_4^{2-} and PO_4^{3-} should be absent. The error is $\simeq 2\%$.
K. SAITO

4612. **4-(2-Pyridylazo)resorcinol as a reagent for the photometric determination of uranium.** A. I. Busev and V. M. Ivanov. *Vestn. Moskov. Univ., Ser. Khim.*, 1960, No. 3, 52–60.—The complex of 4-(2-pyridylazo)resorcinol (**I**) with U obeys Beer's law and the molar ratio of U to reagent in the complex is 1:1. *Procedure*—The test soln. (containing up to 2 mg of U) is diluted to 20 to 25 ml and the pH is adjusted to 7 to 8; 3 ml of a 0·05% soln. of **I** is added, the vol. is adjusted to 50 ml and the extinction is measured at 510 mμ. Under these conditions Cu, Cr, Sn, Bi^{III}, Hg^{I}, Sb^{III}, Sb^{V}, Fe^{II}, Fe^{III}, La and high concn. of Th form ppt. Cobalt, Ni, Mn, Zr, Zn and small amounts of Th form complexes. Lithium, Na, K, Mg, Ca, Sr, Ba, Be, Ti^{IV}, Nb, Ta, Sn^{II}, Sn^{IV}, Mo, W, Ce^{III}, Ce^{IV}, Ir, Rh, As and Se do not interfere.
A. BURWOOD-SMITH

4613. **Extraction-photometric method for the determination of uranium with arsenazo III.** V. I. Kuznetsov and S. B. Savvin. *Radiokhimiya*, 1960, **2** (6), 682–686; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D95.—Small amounts of UO_2^{2+} are determined with arsenazo III (**I**), by extraction with butanol of a compound formed between UO_2^{2+} and **I**, in the presence of diphenylguanidine (**II**), from soln. containing EDTA (**III**). The extraction is possible over a range of acidity from pH 3 to 0·1N to 0·2N-HCl. The mol. extinction coeff. of the complex at 660 mμ is $\simeq 10^5$. For the determination of UO_2^{2+} in soln. containing 1 to 50 μg of UO_2^{2+}, 2·5 ml of 5% **III** soln., 1 ml of 0·05% aq. **I** soln., 0·5 ml of 20% **II** hydrochloride soln. (105 g of **II** dissolved in 80 ml of 6N-HCl and diluted with water to 500 ml) and 5 ml of butanol are added. After separation of the organic layer its extinction is measured at 660 mμ; bivalent cations, Fe^{2+}, Al^{3+}, PO_4^{3-}, F^-, SO_4^{2-}, NO_3^- and Cl^- do not interfere.
A. BURWOOD-SMITH

4614. **Spectrophotometric and potentiometric determination of uranium as the chelate of 8-hydroxyquinoline in a mixed solvent. Fresenius systematic analysis of the cations and use of 8-hydroxyquinoline.** A. R. M. Al-Salihy. *Dissert. Abstr.*, 1961, **21** (8), 2091–2092.—The 8-hydroxyquinolinates of Al, Fe^{III}, Bi, UO_2^{2+} and Ti have been prepared and their solubilities at 26° to 27° in acetone, ethanol, acetone-water and ethanol-water determined. For the spectrophotometric determination of U in acetone-water soln., 460 mμ was a suitable wavelength. With soln. of the aluminium complex in ethanol-water, potentiometric titration with HCl gave a relative error of 2·75%, but titration with NaOH was unsatisfactory. With soln. of the uranyl complex in acetone-water, titration with NaOH gave a relative error of 0·5%, but titration with HCl was unsatisfactory. The separation of small amounts of U from ores, and its conversion into the complex for analysis, is discussed. The properties of the complexes of the cations that can be pptd. with 8-hydroxyquinoline from acetic acid-ammonium acetate buffers have been studied, and their identification by u.v. fluorescence and solubility in acetone or ethanol is discussed. Silver, Hg^{I} and Pb^{II} can be identified without the use of 8-hydroxyquinoline by the effect of u.v. radiation on their chlorides, but the chelates can also be used for identification if certain interfering cations are absent. Spot tests for Cd^{II}, Zn^{II} and Al^{III} were reliable at very low concn.
R. E. E.

4615. **X-ray fluorescence spectrographic determination of uranium.** H. I. Shalgosky and J. Watling (U.K.A.E.A. Res. Group, C.37, Royal Arsenal, Woolwich, London, S.E.18). A.E.R.E. Report AERE-R3666, 1961. 7 pp.—The development of a procedure for the analysis of low-grade ores is described. Results are given for experiments in which an internal standard of Mo and an X-ray tube with a tungsten target were used, and for others in which an internal standard of Sr and a molybdenum-target tube were used; the first method is preferred, as a few ores already contain Sr. Particular attention was given to reducing the particle size of the sample and the results of analyses were in good agreement with those of fused mixtures of ore and $Na_2B_4O_7$ containing an

internal standard of Sr. The method is applicable to ores with contents of U down to 200 p.p.m.
G. J. HUNTER

4616. **Determination of uranium in low-grade ores by an X-ray spectrographic technique.** J. Watling (U.K.A.E.A. Res. Group, C.37, Royal Arsenal, Woolwich, London, S.E.18). Analytical Method AERE-AM81, 1961. 7 pp.—The development of the method is described in AERE-R3666 (Shalgosky and Watling, *Anal. Abstr.*, 1961, **8**, 4615). A riffled sample of the ore is ground under ether in an agate mortar, and, after being dried, 0·5 g is added to 1·5 g of a molybdenum internal standard (prep. described) (≡0·0015 g of MoO_3) and the two are ground together under ether, and dried. The mixture is then examined with a Philips X-ray spectrograph and the content of U is derived from the intensities of the U L_{α_1} and Mo K_α lines and a calibration graph. The method is applicable to ores with contents of U from 200 to 10,000 p.p.m.
G. J. HUNTER

4617. **Complexometric titration of uranium(IV).** J. Korkisch (Anal. Inst. Univ., Wien, Austria). *Anal. Chim. Acta*, 1961, **24** (4), 306–310 (in German).—Dissolve the sample in 10N-HCl (10 ml), add 2 or 3 zinc granules, and after the reduction swirl the open flask until the pure green colour of U^{4+} appears (1 to 2 min.). Make up to 100 ml. Dilute an aliquot so that the final soln. is 0·01 to 0·2N in HCl and contains <1 mg of U per ml. Add a 5% soln. of Solochrome black 6BN (C.I. Mordant Black 3) in methanol (1 ml for each 10 ml of the test soln.) and titrate with 0·1M-, 0·01M- or 0·001M-EDTA according to the expected amount of U. Heat in a boiling-water bath before the end-point (blue to red) is reached. The titration error varies from ±0·1 to ±1·0% in the range 100 to 1·0 mg of U. Interference is caused by Sn^{2+}, Bi^{3+}, Cu^{2+}, Zr^{4+}, Hf^{4+} and Th^{4+}.
A. J. BENNETT

4618. **Separation and determination of sexavalent uranium in the presence of quadrivalent uranium and other cations.** J. A. Blay (Com. Nac. Energía Atómica, Buenos Aires). *An. Asoc. Quim. Argentina*, 1960, **48** (4), 188–203.—The U^{6+} are separated from U^{4+}, Fe^{2+}, Fe^{3+}, V^{3+}, V^{4+}, V^{5+}, Mo^{4+}, Mo^{5+} and Cu^{2+} by passage through a column of a cation-exchange resin and elution with a mixture of H_2SO_4 and H_3PO_4, and then determined photometrically by the peroxide method. The total U may be determined after oxidising the U^{4+} with Fe^{3+}. The method is suitable for analysis of the liquids from the extraction of uranium minerals.
L. A. O'NEILL

4619. **Separation of sub-microgram amounts of uranium from milligram amounts of iron, aluminium and plutonium.** D. G. Boase and J. K. Foreman (U.K.A.E.A., Windscale Works, Calderbridge, Cumberland, England). *Talanta*, 1961, **8** (4), 187–190 (in English).—The determination of U in soln. containing 0·05 to 1·0 μg of U per ml in 1M to 2M-HNO_3 can be carried out by direct fluorimetry if the usual contaminating metals, *viz*, Fe (0·02 to 0·03M), Al (0·01M) and Pu (0·001 to 0·005M) are largely removed. This has been achieved by making the soln. 10 to 11N with respect to HCl in the presence of HI and separating the reduced metals (Fe^{II}, Al^{III} and Pu^{III}) from U^{VI} by passing the soln. through a column of anion-exchange resin (De-Acidite FF). The U^{VI}, retained on the column and subsequently eluted with 0·1M-HCl, was contaminated with <0·4 μg of Pu, <5 μg of Al and insufficient Fe to cause quenching effects in the fluorimetric analysis.
G. S. ROBERTS

4620. **Separation of uranium and thorium on a chromatographic column.** A. M. Petrov, I. A. Korshunov and V. A. Sidorov. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1960, (1), 24–29; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D54.—The method is based on extraction of one component of the mixture with cationite KU-1 or anionite AV-16, with subsequent elution of the adsorbed ion with appropriate soln. The Cl^- forms of the anionites EDE-10P and AV-16 adsorb very little Th from soln. 0·005 to 0·2M in H_2SO_4, but quantitatively extract U; the adsorption capacity for U is greater with AV-16 than with EDE-10P. For the separation, pass the soln. (0·01M in H_2SO_4) at a rate of 0·5 ml per min. through a column containing 0·5 g of AV-16, checking the Th content of the filtrate by the UX_1 activity; 55 ml of 0·8N-HCl elutes 99% of the adsorbed U, and simultaneously converts the resin into the Cl^- form for further use. The H^+ forms of cationites KU-1 and KU-2 selectively adsorb Th from acetate buffer mixtures, the adsorption capacity changing with the pH of the buffer to a maximum at pH 4·2. At this pH, very little U is adsorbed by KU-1. For the separation, pass the acetate buffer (pH 4·2) containing U and Th at a rate of 0·5 ml per min. through a column containing 0·5 g of KU-1. The small amount of adsorbed U is eluted with 35 ml of acetate buffer (pH 5·37). Then elute the Th with 4N-HCl at a rate of 0·3 ml per min. Uranium is determined by colorimetry of soln. of $(UO_2)_2$-$[Fe(CN)_6]$ at pH 1·24 to 1·42.
C. D. KOPKIN

4621. **Volumetric determination of uranium in the presence of high concentrations of iron.** T. J. Blalock (Bur. of Mines, Washington, D.C., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. BM-RI-5687, 1959. 11 pp.—Results are given of an investigation conducted to develop a more accurate procedure for determining small amounts of U in the presence of large amounts of Fe in materials such as shale or black sands. Results indicated that, by the use of double precipitation of UF_4 from reduced acid soln., concn. as low as 0·1 to 0·2 mg of U per 100 ml of soln. could be quantitatively separated, provided that a suitable carrier was present and NH_4Cl was present to prevent peptisation. Uranium was determined by titration with $Ce(SO_4)_2$.
NUCL. SCI. ABSTR.

4622. **Polarography of uranium(VI) - EDTA complexes.** D. G. Davis (Dept. of Chem., Louisiana State Univ., New Orleans, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 492–494.—Sexavalent U may be determined polarographically in a basal soln. 0·1M in EDTA and 1·0M in $NaClO_4$. At pH <5 a ppt. of uranyl - EDTA forms, while at pH >7·5 the complex decomposes. Conditions are optimum at pH 5·5. Zinc, Ni^{2+}, Co^{2+}, Al^{3+}, Cd^{2+}, Mg^{2+}, Pb^{2+}, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-} at concn. 2 to 4 times that of the U do not interfere. Copper and PO_4^{3-} should be absent, and in the presence of Cu preliminary solvent-extraction of U is recommended.
T. R. ANDREW

4623. **Radiometric method for the determination of uranium in solutions containing ionium [thorium-230].** N. N. Shashkina. *Atomnaya Energiya*, 1961, **10** (4), 392–393.—Soln. of uranium ores may

contain ^{230}Th, which interferes with the determination of U by measurement of the α-emission. This interference can be avoided by a preliminary measurement of the β-emission of the sample and application of a correction (Evans, *Phys. Rev.*, 1934, **45**, 38). Results compare well with those obtained chemically. J. W. PRICE

4624. **Determination of iron, nickel and copper in metallic uranium by extraction and spectrography.** Shizo Hirano, Hitoshi Kamada and Hitoshi Sato (Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1960, **9** (2), 168–172.—Iron (2 to 200 p.p.m.), Ni (40 to 100) and Cu (2 to 20) are extracted as their diethyldithiocarbamates with $CHCl_3$ (Lacoste *et al.*, *Anal. Chem.*, 1951, **23**, 871) from an aq. soln. at pH 2·4 in the presence of a large amount of U (≃1 g). The extracted metals are converted into chlorides and applied to a porous graphite electrode (diam. 6 mm) treated with silicone varnish for a.c. spark excitation. The lines Fe 3047·605, Ni 3134·108 and Cu 3247·54 are compared with the internal standard Mo 3132·594 (for Fe and Ni) and 3193·97 (for Cu).
K. SAITO

4625. **Determination of trace impurities in metallic uranium. VI. Photometric determination of trace amounts of cobalt.** Masami Suzuki and Tsugio Takeuchi (Fac. of Engng, Nagoya Univ., Chikusa-ku, Nagoya). *Japan Analyst*, 1960, **9** (2), 179–181.—Cobalt is extracted with Na diethyldithiocarbamate (**I**) and determined with nitroso-R salt (**II**). Nickel and Cu are also extracted but do not interfere. The excess of **II** is decomposed with H_2O_2. *Procedure*—Dissolve the sample (1 g) in HNO_3 (3 ml), add citric acid soln. (25%) (10 ml) and make the soln. ammoniacal (vol. ≃25 ml); add **I** soln. (2%) (2 ml) and extract with CCl_4 (3 × 15 ml). Evaporate the org. layer to dryness, heat to white fumes with H_2SO_4 and HNO_3 (3 drops each), cool, add water (5 ml), adjust the soln. to pH 6 with Na acetate soln. (10%), add **II** soln. (0·2%) (0·5 ml), heat on a water bath for 10 min., add HCl (6N) (3 ml) and H_2O_2 soln. (30%) (3 drops), heat for 30 min. on a water bath and dilute to 15 ml for photometry at 420 mμ.
K. SAITO

4626. **Determination of plutonium in reactor fuel processing and effluent plant solutions (rapid lanthanum fluoride co-precipitation).** U.K.A.E.A. (Production Group, Tech. Branch, Windscale, Cumberland, England). U.K.A.E.A. Report PG 199(W), 1961. 6 pp.—The procedure, for which full experimental details are given, involves reduction to Pu^{III} with hydroxyammonium chloride and co-pptn. of PuF_3 with LaF_3. The mixed ppt. is dried and α-counted. The method is not specific for Pu, as other α-emitters (*e.g.*, Th, U and Am) contribute to the measured activity.
G. J. HUNTER

4627. **Determination of plutonium by mass spectrometry using a plutonium-242 tracer.** R. K. Webster, A. A. Smales, D. F. Dance and L. J. Slee (Anal. Chem. Branch, A.E.R.E., Harwell, Berks., England). *Anal. Chim. Acta*, 1961, **24** (4), 371–380 (in English).—The Pu analysed contained only 0·005 to 0·01% of ^{242}Pu. All the Pu soln. were prepared at concn. of ≃0·1 μg of Pu per g in 3N-HNO_3. *Procedure*—Mix the tracer soln. (2 g) and sample soln. (2 g) and evaporate to dryness. Dissolve in 0·1% hydroxyammonium chloride in N-HCl, add 20% (w/v) hydroxyammonium chloride (3 drops), evaporate and warm the residue with conc. HNO_3 (2 ml). (This brings ^{239}Pu and ^{242}Pu into the same valency state and ensures isotopic equilibration.) Evaporate, dissolve in 8N-HNO_3 (2 ml) and transfer to a column of De-Acidite FF (40 mg). Wash with 8N-HNO_3 to remove U, and elute Pu with 0·1% hydroxyammonium chloride in 1·0N-HCl. Evaporate the eluate to dryness, add conc. HNO_3 and again evaporate. Transfer the residue with a small amount of water to the sample filament of a mass spectrometer. Then calculate the total Pu by means of an equation. The precision for an aliquot containing 0·1 μg of Pu is ±0·6%.
A. J. BENNETT

4628. **Radiochemical determination of promethium-147 in fission products.** R. D. Britt, jun. (Savannah River Lab., E.I. du Pont de Nemours & Co., Aiken, S.C., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 602–604.—Samples of neutron-irradiated natural uranium which had been allowed to decay for periods between 120 days and 5 yr. have been examined. Yttrium is extracted from 1·65M-HNO_3 soln. with di-2-(ethylhexyl) hydrogen phosphate (**I**) in Ultrasene (an inert diluent) and rejected. Cerium and Pm are separated from Cs and Sr by extraction with **I** from 0·05M-HNO_3 soln., and Pm is subsequently stripped from the organic extract into 10N-HNO_3 after oxidation of Ce^{III} to Ce^{IV} by $NaBrO_3$. Promethium and any ^{106}Rh are counted in a liquid scintillation counter, corrections being made for their different β-spectra.
T. R. ANDREW

4629. **Specific micro-diffusion method for the determination of fluorine based on the lanthanum - alizarin complexan colour system.** F. J. Frere (Toxicol. Sect., Office of Medical Examiner, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 644–645.—Hydrofluoric acid liberated by H_2SO_4 treatment of the sample soln. in a plastic Conway unit is absorbed in dilute NaOH soln. The absorbent soln. is adjusted to pH 5·4 and equal volumes of 0·001M-$La(NO_3)_3$ and 0·001M-alizarin complexan (1,2-dihydroxyanthraquinon-3-yl-methylamine-*NN*-diacetic acid) are added. In the presence of F^-, the colour changes from wine-red to lilac blue. The soln. is diluted to a suitable vol. and, after at least 1 hr., the extinction is measured at 615 mμ. As little as 0·25 μg of F^- may be detected.
T. R. ANDREW

4630. **Application of gas - liquid chromatography to the analysis of corrosive gases. I. Development of apparatus and technique for the separation of mixtures of chlorine trifluoride, hydrogen fluoride and uranium hexafluoride.** G. Iveson (U.K.A.E.A., Capenhurst, England). U.K.A.E.A. PG Report 82 (CA), 1961. 15 pp.—Full details are given for the construction of apparatus suitable for the analysis of diffusion-plant gases. A sample of 20 ml is suitable and the lower limit with the equipment used is ≃5%. The column consists of a mixture of "Kel-F" oil and "Kel-F" powder (1:5) in a nickel tube (200 cm long and 0·25 in. internal diam.) at 60°. Katharometer detection is used. The carrier gas is generally helium at 40 ml per min. Nitrogen is preferred for the resolution of ClF_3 and HF, the latter giving a negative peak.
G. RUSSELL

4631. **Potentiometric determination of bromide and thiocyanate in one operation with silver nitrate and the silver electrode.** M. Scheibitz (Agfa

Akt.-Ges., Wolfen, Germany). *Z. wiss. Photogr.*, 1960, **54**, 46–51.—Bromide and SCN^- cannot be separated by potentiometric titration with $AgNO_3$ in aq. soln. because the solubility products of the silver salts are too near together, but a separation can be effected by titration in gelatin soln. (0·05 to 0·5%) if the Br^- concn. is equal to or greater than the SCN^- concn. Two distinct breaks appear in the titration curve. The reason for the greater separation of the pptn. potentials in the presence of gelatin is that the specific surface of the AgBr is relatively large compared with that in the aq. soln. and Br^- are more strongly adsorbed in the presence of gelatin than are SCN^-. Chloride can be determined in the gelatin soln. if correction is made for the original Cl^- content of the gelatin. The application of the method to the determination of Br^- and SCN^- in a developer is illustrated.

CHEM. ABSTR.

4632. **Detection of the complex anions I_3^-, I_2Cl^-, I_2Br^- and Br_3^- with Brilliant green.** L. N. Lapin. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 323–327; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D47.—The detection of iodine with dyestuffs of the di- and tri-phenylmethane series was studied. Best results were obtained with Brilliant green (C.I. Basic Green 1) (**I**). An aq. ethanolic soln. of **I** in the presence of iodine forms intense blue - green salts with I^-, Cl^- and Br^-, which are soluble in benzene and toluene. To detect iodine as I_2Cl^-, to 10 ml of test soln. add 2 g of NaCl, 1 ml of 5N-HCl and 0·5 ml of a 0·5% nitrite soln.; after 2 to 3 min. add 0·5 ml of a 0·5% soln. of **I** in 25% ethanol, shake, and immediately add a few ml of benzene or toluene. In the presence of I^-, the org. layer is coloured blue - green. Beer's law is obeyed with a content of <100 μg of KI for 10 ml of toluene. Carbon tetrachloride and ethyl ether may also be used as solvents, and methyl violet or crystal violet instead of **I**. The sensitivity of detection of I^- is a few tenths of 1 μg; Br^- do not interfere. The interference of $SbCl_6^-$, $AuCl_4^-$, $TlCl_4^-$ and $FeCl_4^-$ is avoided by treating the sample with an alkali carbonate or CaO. Organic substances present are removed by igniting the sample. The method can be used for the micro-determination of iodine in sodium chloride, water from mine-shafts and water supplies, and of I^- in standard NaCl and KCl reagents. C. D. KOPKIN

4633. **Oxidation and reduction reaction involving complex formation. VIII. Amperometric titration of manganese with triphosphate.** Toyokichi Kitagawa (Chem. Dept., Fac. of Education, Kobe Univ., Higashinada-ku, Kobe). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 83–85.—Bivalent Mn (1 to 10 mg) is rapidly (<30 sec.) oxidised to Mn^{III} with $KMnO_4$ in the presence of triphosphate (2 g) at pH 6·5 to 7·0. The amperometric titration is best effected with a rotating platinum electrode (600 r.p.m.) at +0·35 or +0·75 V *vs.* the S.C.E. in the presence of Triton-X-100. The error is 0·5% and the presence of Co (<15 mg), Ni (<20 mg), Fe (<2 mg) or Cr (<5 mg) per 3 mg of Mn does not vitiate the estimation.

IX. Polarographic determination of manganese in the presence of a large amount of nickel and cobalt by the use of triethanolamine and potassium cyanide as complexing agent. Toyokichi Kitagawa. *Ibid.*, 1960, **81** (4), 572–575.—Interference of Co, Ni and Fe in the polarographic determination of Mn (<1 millimole per litre, $E_{\frac{1}{2}} = -0.55$ V) in triethanolamine (**I**) (2 to 10 ml per 25 ml) soln. is eliminated by the addition of KCN (0·1 to 0·5M), the $E_{\frac{1}{2}}$ values of the cyanide complexes of Co^{III}, Ni and Fe being −1·6, −1·3 and −0·8 V *vs.* the S.C.E., respectively. The sample soln. containing Mn and ≃10 times its wt. of Co, Ni and Fe is mixed with **I** (5 ml), N-NaOH (5 ml), M-KCN (10 ml) and 0·1% gelatin soln. (5 drops), made up to 25 ml, bubbled with air (to oxidise Co^{II} to Co^{III} and Mn^{II} to Mn^{III}) and the polarogram recorded.

K. SAITO

4634. **Determination of manganese in the systems manganese(II) - iron(III) and manganese(II) - aluminium(III) with EDTA (disodium salt).** V. A. Rad'ko and E. M. Yakimets. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 166–175; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D105.—Bivalent Mn is not oxidised by atmospheric oxygen at pH 8·5 to 9 in ammoniacal acetate buffer soln., and Na K tartrate can be used to mask Al^{3+} and Fe^{3+} in the determination of Mn^{2+} with EDTA (disodium salt) (**I**). On this basis, a method is developed for the determination of Mn^{2+}, Al^{3+} and Fe^{3+}, when present together. To determine Fe, add 5% aq. NH_3 to an acid soln. of the sample until the soln. is turbid, then add 5 ml of N-HCl and 1 ml of sulphosalicylic acid, dilute to 50 ml, heat to 50° to 60°, and titrate with **I** soln. till the colour of Fe sulphosalicylate is discharged. To determine total Al^{3+} and Mn^{2+}, add excess of **I** to the soln. obtained after the titration of the Fe, heat to boiling, neutralise to Congo red with 5% aq. NH_3, add 10 ml of acetate buffer soln. (pH 6), cool, dilute to 100 ml and titrate the excess of **I** with Fe^{3+} soln. to the brick-yellow colour of Fe sulphosalicylate. To determine Mn^{2+}, neutralise a separate aliquot of the soln. to methyl orange with buffer soln. (pH 8·5 to 9) (to 500 ml of 25% aq. NH_3 add 300 ml of glacial acetic acid and dilute to 1 litre; to check the capacity of the buffer mixture, dilute 5 ml to 100 ml and titrate to phenol red with N-HCl; this should take 6 to 7 ml; if less, add the calculated amount of conc. aq. NH_3 to the buffer soln. and again check the capacity of the soln.); add 15 ml of 28% Na K tartrate soln. and 5 ml of the same buffer soln., dilute to 100 ml, add 5 or 6 drops of Fast mordant blue B (C.I. Mordant Blue 13), and titrate Mn^{2+} at 10° to 18° with **I** soln. If the sum of Fe plus Al in the soln. being titrated is <10 mg, reduce the vol. of Na K tartrate soln. to 5 ml. The colour change at the end-point is satisfactorily sharp if the amount of Fe plus Al is <30 mg. C. D. KOPKIN

4635. **Determination of metallic manganese in slags and agglomerates.** V. S. Nagibin and A. V. Arkhipova. USSR Pat. 134,055 (10.12.1960).—*Procedure*—Boil 200 ml of 2·5% $CuSO_4$ soln. for 5 to 10 min. with 0·5 g of slag, filter, and wash the residue with hot water. To the filtrate add 5 ml of H_2SO_4 (1:1) and precipitate the Cu with aluminium foil while boiling. When the soln. is colourless, filter off the excess of aluminium and the pptd. Cu, wash the ppt. with hot water, cool the filtrate and make it up to 250 ml. To 25 ml of this soln. add 25 ml of water, 20 ml of H_2SO_4 (1:1), 10 ml of H_3PO_4 (sp. gr. 1·7) and 10 to 15 ml of 1·5% $AgNO_3$ soln., heat, and to the hot soln. add 20 to 25 ml of 20% $(NH_4)_2S_2O_8$ soln. and boil for 4 to 6 min. Cool, and titrate with 0·1N-$(NH_4)_2SO_4.FeSO_4$ to a pale pink, add 3 to 4 drops of 0·2% *N*-phenylanthranilic acid soln. and complete the titration. C. D. KOPKIN

4636. **Cerimetric method for the assay of pyrolusite.** M. R. Verma, S. K. Mathur, P. Dayal and S. Adwani (Nat. Phys. Lab., Hillside Road, New Delhi,

India). *Z. anal. Chem.*, 1961, **180** (3), 181–184 (in English).—*Procedure*—Digest the ore (0·8 g, 100 mesh) with N-oxalic acid (25 ml), H_2SO_4 (10 ml) and H_2O (to ≃150 ml) till dissolution of black particles is complete. Filter the soln. from SiO_2 and dilute to a suitable vol. Titrate aliquots at 50° to 60° with 0·1N-Ce^{4+} (prep. described), with ferroin as indicator; 20% HCl (25 ml) may be added to the soln. being titrated, except when much Fe is present. Results for 9 samples (50 to 94% of MnO_2) were generally within 0·1% of those by the $KMnO_4$ method. G. RUSSELL

4637. **Flame-photometric determination of iron in metal ingots, limestone, slag and dolomite with the aid of extraction with isobutyl methyl ketone.** Hidehiro Goto and Emilo Sudo (Inst. Iron, Steel and other Metals, Tohoku Univ., Katahira-cho, Sendai). *Japan Analyst*, 1960, **9** (3), 213–215.—Iron (<0·02%) in metallic aluminium, lead or copper, limestone or dolomite is extracted from soln. in 6N-HCl with isobutyl methyl ketone and determined flame-photometrically at 372 mμ (pressure of H, 2 lb per sq. in., and O, 18 to 20 lb per sq. in.). The working curve is linear for <7 μg of Fe per ml of the org. soln. K. SAITO

4638. **Quantitative determination of metallic iron in the presence of iron oxides in treated ores and slags.** M. G. Habashy (25 Sultan Hussein Street, Alexandria, Egypt). *Anal. Chem.*, 1961, **33** (4), 586–588.—Existing methods are reviewed and a new procedure is proposed. Weigh the sample (0·2 to 1·0 g) into a conical flask containing 20 ml of water. Add $CuSO_4.7H_2O$ (10 g) and mercury metal (1 ml) and boil. Stopper the flask, allow to cool to room temp. and shake for 1 to 4 hr. Filter through filter-paper, wash the residue free from Cu^{II}, then dissolve it in HNO_3 (5%) (100 ml). Determine the Cu content of this soln. electrolytically and calculate the Fe that has been displaced. If any other metals are suspected to be present they should be determined in the main copper sulphate filtrate and the calculated Fe content corrected accordingly. T. R. ANDREW

4639. **Spectrophotometric determination of ferric iron.** G. Ceriotti and L. Spandrio (Centro Studio Tumori di Busto, Arsizio, Italy). *Anal. Chem.*, 1961, **33** (4), 579–580.—In soln. of pH 2 to 3, Fe^{III} (1 to 20 μg) gives a red colour (max. absorption at 515 and 552 mμ) with *p*-amino-*NN*-dimethylaniline, which is stable for 6 min., and has a molar extinction coefficient of 9500. Quadrivalent Ce and Mn^{VII} interfere seriously, while Cu^{II}, Ag, Hg^{II} and Mn^{II} interfere only slightly. Pyrophosphate must be absent. T. R. ANDREW

4640. **Rapid determination of iron in high-purity titanium slag.** Tsuyoshi Nakayama, Takashi Amako and Akira Hirono (Osaka Titanium Co., Higashihama, Amagasaki, Hyogo-ken). *Japan Analyst*, 1960, **9** (2), 119–123.—Iron in concn. <5% is extracted with H_2SO_4 from the fused sample and determined photometrically with KSCN in the presence of $(NH_4)_2S_2O_8$; Ti (<250 mg), Cr (<0·5 mg) and V (<0·5 mg) do not interfere. The working curve is linear for <2·0 mg of Fe per 250 ml. The standard deviation is ±0·08% (absolute) for 2·5% of FeO, and the time taken for a determination is 50 min. *Procedure*—Fuse the sample (0·5 g) with KOH (3·5 g) and H_2BO_3 (1·5 g) at 400° to 800° for 15 min. Extract the melt with hot water (80 ml), add H_2SO_4 (1:1) (50 ml) after 10 min. and heat with H_2O_2 soln. (3%) (a few drops). Cool, dilute to 250 ml, and to a 25-ml portion add H_2SO_4 (1:1) (10 ml), 0·1N-$KMnO_4$ (until a pink colour remains), $(NH_4)_2S_2O_8$ soln. (2%) (10 ml) and KSCN soln. (20%) (10 ml), and make up to 250 ml. Measure the extinction at 500 mμ. K. SAITO

4641. **Determination of ferrous oxide in small samples of tourmaline.** I. I. Gekht and S. I. Potok. *Vestn. Akad. Nauk KazSSR*, 1960, (9), 68–71; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D108.—The sample is decomposed with a mixture of H_2SO_4, H_3PO_4 and V_2O_5 (soln. *A*), simultaneously oxidising Fe^{2+} to Fe^{3+}, and the excess of V^V in the resulting soln. is titrated with a soln. of $(NH_4)_2SO_4.FeSO_4.6H_2O$. To prepare soln. *A*, dissolve 2 g of V_2O_5 in a mixture (2:1) of conc. H_2SO_4 and H_3PO_4 and dilute to 1 litre. Evaporate 5 ml of this soln. till V_2O_5 begins to crystallise, add 5 ml of the mixture of acids, and again heat to dissolve the V_2O_5. To the resulting soln. add 20 to 25 mg of the finely ground tourmaline and dissolve it by stirring, slowly raising the temp., for 10 to 15 min. Dilute the soln. till it is 6N in H_2SO_4, add 1 to 2 drops of a soln. of *N*-phenylanthranilic acid (**I**) (dissolve 0·03 g of **I** in 30 ml of water containing 0·03 g of Na_2CO_3 and make up to 100 ml), and titrate with 0·02N-$(NH_4)_2SO_4.FeSO_4.6H_2O$ till the violet colour becomes pale green. Carry out a blank at the same time with the same amount of soln. *A*. Determine the content of Fe by difference. The relative error of the determination is within ± 9%. C. D. KOPKIN

4642. **Neutron activation analysis and its application in the analysis of steel.** W. Reiser and H. Schneider (Phys. Inst., Univ., Giessen, Germany). *Arch. Eisenhüttenw.*, 1961, **32** (1), 31–38.—The application of this technique to steel and the necessary stages of an analysis are discussed. An examination of the spectrum of steel (by a scintillation counter and hundred-channel spectrometer) indicated that only Mn, Cu, Cr and Mo could be determined without chemical separation, Mn immediately after irradiation and Cu, Cr and Mo after a few hours or days to allow for the decay of the activity. Carbon, Si, P and S can be determined by means of the β-activity only, and chemical separation is necessary; Ni and Ti can be determined quantitatively only after chemical separation. Aluminium can be determined immediately after irradiation, but for both Ti and Al the determination is made difficult by the short half-life value. (24 references.) M. LAPIDOT

4643. **Error of gas analysis due to insertion of steel samples through the mercury lift.** Saburo Yanagisawa and Michiharu Seki (Fac. of Engng, Keio Univ., Koganei, Tokyo). *Japan Analyst*, 1960, **9** (2), 176–177.—When the sample is inserted through a mercury lift (diam. 10 mm), the O content becomes greater, whilst that of N remains unchanged. Contamination appears to take place while the sample is floating on the surface of the mercury. K. SAITO

4644. **Studies on chemical analysis by the use of organic reagents. V. Determination of copper and nickel in iron and steel.** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *Japan Analyst*, 1960, **9** (4), 272–275.—Both Ni (<10 μg) and Cu (<10 μg) are extracted from strongly basic soln. with 1,2-di-(*o*-aminobenzylideneamino)ethane (**I**) in benzene and determined from the extinctions at 416 and 486 mμ. With

iron and steel (0·1 g sample), the HCl or HNO_3 soln. is mixed with tartrate (0·4 g), neutralised with N-NaOH and made ammoniacal (3 ml of conc. aq. NH_3), and the Cu is extracted with **I** (0·01%) in benzene for the photometric examination. Nickel (<0·03%) does not interfere. For Ni, a soln. of the sample (40 mg) is mixed with tartaric acid (1 g) and a 5 to 10-ml excess of N-NaOH, heated with 0·1% **I** in ethanol for 10 min. and extracted with benzene. K. SAITO

4645. **Determination of trace elements in iron and steel. I. Determination of zinc in iron and mild steel by dithizone extraction followed by polarography.** Shizuya Maekawa, Yoshio Yoneyama and Eiichi Fujimori (The Japan Steel Works, Muroran, Hokkaido). *Japan Analyst*, 1960, **9** (3), 244–247.—When Zn (>0·001%) is extracted with dithizone (**I**) in $CHCl_3$ from a citrate buffer (pH 8·0 to 8·3), Cu, Ni and Co are also extracted, but only a negligible amount is transferred into HCl soln. Small amounts of Ni and Cu do not interfere with the polarography of Zn in NH_4Cl soln. containing aq. NH_3 in the presence of gelatin. The wave of Co overlaps that of Zn, but there is no interference when the Co in the sample is <0·3%. The error is <3%, and the time taken is 40 min. *Procedure*—Heat the sample (1 g) with HNO_3 (5 ml) and $HClO_4$ (60%) (20 ml) until white fumes appear, dissolve the residue in water (50 ml), filter, dilute the filtrate to 100 ml, add citric acid soln. (50%) (20 ml), adjust the pH to 8·2 with aq. NH_3 and shake the soln. with **I** in $CHCl_3$ (0·1%) (20 ml) for 1 min. Repeat the extraction until the organic layer remains green. Wash the extract with aq. NH_3 (1:1000), then shake it with HCl (0·1N) (20 ml) to transfer the Zn into the aq. layer. Wash the HCl with $CHCl_3$ (5 ml), expel $CHCl_3$ and make up the soln. to 50 ml with the supporting electrolyte (273 g of NH_4Cl and 330 ml of conc. aq. NH_3 per litre) (10 ml) and gelatin soln. (0·1%) (2 ml) for polarography.

II. Determination of cobalt by solvent extraction followed by photometry. Shizuya Maekawa, Yoshio Yoneyama and Eiichi Fujimori. *Ibid.*, 1960, **9** (6), 475–479.—Cobalt (0·0005 to 0·1%) is extracted with isobutyl methyl ketone (**II**) and benzene as the phenazone - thiocyanate complex (Sudo, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1953, **74**, 658), Cu being masked with oxalate; Fe is previously extracted with butyl acetate (**III**). The coloured soln. (max. absorption 625 mμ) is stable. The time taken for 5 samples is 2 hr. *Procedure*—Dissolve the sample (≃1 g, containing <0·3 mg of Co) in aqua regia (10 ml), heat to white fumes with $HClO_4$ (15 ml) and HF (a few drops) (add HCl during heating when Cr is present), and dissolve the product in HCl (20 ml) and water (5 ml). Shake the soln. with **III** (20 ml) for 1 min., wash the org. layer with HCl (2:1) (5 ml), heat the aq. layer to expel **III**, add HNO_3 (1 ml), heat with H_2SO_4 (1:1) (2 ml) and water (10 ml), cool, add satd. oxalic acid soln. (10 ml) and NH_4SCN soln. (15%) (15 ml), and aq. NH_3 (1:1) to give a pH of 2·0, then add phenazone soln. (10%) (5 ml) and dilute to 50 ml. Shake the soln. with a mixture of **II** and benzene (1:1) for 1 min. and examine photometrically. K. SAITO

4646. **Spectrophotometric determination of acid-soluble aluminium in steel.** Mutsumi Ihida (Nippon Steel Tube Co., Minami-watarida-cho, Kawasaki). *Japan Analyst*, 1960, **9** (3), 209–213.—Acid-soluble Al (<0·03%) in steel is separated from Al in other forms by dissolving the sample in dil. HNO_3. Spectrographic analysis is effected with a porous carbon electrode by intermittent d.c. arc excitation (220 V, 6 amp.; interruption factor, 1/3; period, 0·5 sec.; preliminary discharge, 5 sec.; exposure, 1 min.). The line pair is Al 3961·53 - Fe 3977·74. *Preparation of the sample soln.*—Dissolve the sample (1 g) in HNO_3 (1:1) (20 ml) and KNO_3 (1·3 g), evaporate the soln. then make it up to 10 ml, and filter through dry paper. Add 0·15 ml of this soln. to a crater (diam. 3 mm, depth 3 mm) in a carbon electrode (diam. 5 mm, length 25 mm). K. SAITO

4647. **Rapid determination of silicon in steel.** M. del Carmen Consuegra Ferrer and R. de la Cierva. *Inst. Hierro Acero*, 1961, **14**, 392–396.—A colorimetric method, suitable for carbon, silicon and silicon - manganese high-elasticity steels, and for concn. of Si from 0 to 0·1, 0·1 to 0·4, or 0·4 to 3%, is described. The sample, dissolved in HNO_3, is treated with ammonium molybdate soln., the ppt. is dissolved in H_2SO_4 and reduced with $(NH_4)_2SO_4.FeSO_4$ soln. and the blue colour is measured at 678 mμ. L. A. O'NEILL

4648. **Spectrophotometric determination of traces of bismuth in iron and steel.** Shiro Watanabe (Kamaishi Works, Fuji Iron & Steel Co., Kamaishi, Iwate-ken). *Japan Analyst*, 1960, **9** (1), 48–53.—After Fe has been removed by extraction with amyl acetate (**I**), BiI_3 can be pptd. with KI soln. and extracted from a soln. in 6·5N-H_2SO_4 with iso-amyl alcohol (**II**) and determined photometrically at 450 mμ. The excess of iodine is reduced with NaH_2PO_2. The error is <10% for <0·01% of Bi, and <2% for <0·1%. *Procedure*—Dissolve the sample (2 g) in HNO_3 (1:1, 20 ml), heat to dryness, dissolve the residue in HCl (1:1, 20 ml), filter and wash the residue with HCl (1:50). Evaporate the filtrate and the washings, dissolve in conc. HCl (20 ml) and shake with **I** for 2 min. Wash the **I** layer with conc. HCl (5 ml), heat the aq. layer and washings with H_2SO_4 (2:5, 30 ml) to white fumes and make up to 50 ml. To a 25-ml portion add KI soln. (10%, 2 ml) and NaH_2PO_2 soln. (25%, 10 ml), set aside for 30 min. and shake with **II** (10 ml). Measure the extinction at 450 mμ. K. SAITO

4649. **Photometric determination of tantalum in stainless steel by the pyrogallol method.** Kimio Mukaewaki (Nippon Tokushu Steel Tube Co., Funato, Itabashi-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 113–118.—The method of Marzys (*Analyst*, 1955, **80**, 194) was applied to stainless steel. *Procedure*—Dissolve the sample (5 g) in a mixture of HNO_3 and HCl (1:1) (25 ml) and heat with $HClO_4$ (60 ml) to white fumes. Cool, dissolve the residue in water (200 ml) containing 6N-HCl (10 ml), then boil the soln. with Na_2SO_3 (5 g) and filter-pulp for 5 min., set aside at 60° for 30 min., filter, and wash the ppt. with HCl (1:50). Ignite the ppt. in a silica crucible (the use of a platinum dish increases the extinction), heat the ash with H_2SO_4 (1:1) (2 drops) and HF (3 ml) to white fumes, add $KHSO_4$ (5 g) and tartaric acid soln. (15%) (45 ml) and make up to 50 ml. To a 25-ml portion add ammonium oxalate soln. (1·5% in 9N-HCl) (50 ml) and pyrogallol soln. (50 g of pyrogallol, 25 ml of conc. HCl and 10 ml of 2M-$SnCl_2$, made up to 250 ml) (23 ml). Measure the extinction at 420 mμ after 15 min. Titanium (<0·5 mg per 100 ml), W (<3 mg) and Nb (<14 mg) do not interfere. K. SAITO

4650. **Determination of the inter-element effect in the X-ray fluorescence analysis of chromium in steel.** W. Marti (Sulzer Bros., Winterthur, Switzerland). *Spectrochim. Acta*, 1961, **17** (4), 379–383.—Details are given of the principles underlying the exact determination of inter-element effect with the minimum number of operations. A simple transformation of Sherman's relation (*cf. Ibid.*, 1955, **7**, 283) affords a working equation that takes into account the influence of all the elements present. Each of ten equal parts of a chromium rod was melted in an argon atmosphere in a high-frequency furnace with the addition of 5% of another element in each case. The results of wet analyses of these samples, taken together with the measured intensities of the Cr K_α rays and the working equation, provide the required influence coefficients by simple calculation. These values, applied to 24 standard samples, give a working curve which is linear within the limits of accuracy (±2%) of the whole analysis.
E. G. CUMMINS

4651. **Determination of magnesium oxide in non-metallic inclusions in welding steel.** Hidehiro Goto and Shigero Ikeda (Inst. Iron, Steel and other Metals, Tohoku Univ., Katahira-cho, Sendai). *Japan Analyst*, 1960, **9** (2), 182–183.—For the removal of Fe, the sample is chlorinated at 320° to 350° for 1 hr. and the chlorides are dissolved in ethyl acetate, which does not dissolve MgO. The method is improved by dissolving the sample in a mixture of ethyl acetate and bromine (2:1, v/v) (9 ml per 1 g). The residue is filtered off, dissolved in acid and the Mg determined photometrically. The error by the latter method is ≃±5%.
K. SAITO

4652. **Spectrochemical micro-analysis of oxide inclusions isolated from steel.** K. F. Lüdemann, H. W. Fenzke and F. Gruner (Bergakad., Freiberg i. Sa., Germany). *Neue Hütte*, 1960, **5**, 238–244.—A routine method for the quant. analysis of oxide inclusions (*e.g.*, FeO, MnO, Cr_2O_3, Al_2O_3, SiO_2, CaO, MgO and V_2O_5) in steel, in which a Zeiss u.v. quartz spectrograph Q24 and a high-voltage spark generator with a controlled spark discharge are employed, was developed. A rotating (5 r.p.m.) graphite electrode (5 mm diam.) dips 1 to 2 mm into the test soln. (0·5 to 1 mg of inclusions fused with 40 times as much borax, and dissolved in 0·5 to 1 ml of 10% citric acid soln. containing 10·0 mg of Co per ml as internal standard). Excitation and exposure conditions and evaluation of the photographed spectra were investigated. For all oxides, the mean relative error of the separate measurements and of the calibration curve was well below 10%. If given assistance in evaluating the spectra, an experienced analyst can handle 6 to 8 different samples per day.
CHEM. ABSTR.

4653. **Catalytic analysis. IV. Detection of submicro amounts of cobalt by the diphenylcarbazone - hydrogen peroxide, or tiron - diphenylcarbazone - hydrogen peroxide reactions.** J. Bognár and O. Jellinek (Tech. Univ. Miskolc, Hungary). *Magyar Kém. Foly.*, 1961, **67** (4), 143–147.—Cobalt has a strong catalytic effect on the oxidation of diphenylcarbazone by H_2O_2. By this reaction 10^{-3} μg of Co^{2+} can be detected in 5 ml of soln. The effect is much stronger in the presence of tiron, which lowers the limit of detection to 10^{-5} μg of Co^{2+} in 5 ml. Factors which influence the speed of the reactions, *e.g.*, concn. of reagents, temperature, pH (max. 9·5 to 10·5), and the presence of other elements and complex-forming materials, were investigated and the results are given in graphical and tabular form. The following affect the reaction seriously—OsO_4, Ni, Fe and Ca increase the speed; Ba, ethanol and acetone decrease the speed; and ammonia, pyridine, 1-nitroso-2-naphthol and KCN act as catalytic poisons.

V. Contributions to the oxidation of alizarin and alizarin derivatives by sodium perborate and hydrogen peroxide. Detection of cobalt. J. Bognár and O. Jellinek. *Ibid.*, 1961, **67** (4), 147–151.—The reactions named take place at a much higher rate in the presence of Co. The oxidation of alizarin (**I**), Na alizarinsulphonate (**II**), purpurin (**III**) and quinalizarin (**IV**) by H_2O_2 is described in detail. The rates of reactions are influenced by such factors as concn. of reagents, temperature and pH (max. between 11·5 and 12·4). The Co detection limit is 10^{-5} μg per 5 ml of soln. for **I**, **II** and **III**, and 10^{-4} μg for **IV**. The effects of 35 other elements and complex-forming materials on the **III** - H_2O_2 reaction were studied; Ca, Mg, Ni and Ti suppress the catalytic effect of Co; OsO_4 catalyses the reaction similarly to Co; Pb, Pd and Mn accelerate the reaction but suppress the catalytic effect of Co; and complex-forming materials, *e.g.*, 1-nitroso-2-naphthol, pyridine, 2,2′-bipyridyl, KCN, dimethylglyoxime and CO_2 act as catalytic poisons.
B. VASZKO

4654. **Amperometric determination of cobalt as tellurite.** G. S. Deshmukh, V. D. Anand and A. Joseph (Indian Inst. Tech., Agricultural Gardens, Kanpur, India). *Z. anal. Chem.*, 1961, **180** (3), 174–181 (in English).—The pptn. of cobalt tellurite is carried out in a soln. containing KCl (0·1M), gelatin (0·01%) and ethanol (10%). The concn. of the K_2TeO_3 titrant is ≃10 times that of the Co^{2+} being titrated. At an applied potential of −1·5 V *vs.* the S.C.E., both the Co^{2+} and the Te^{4+} are reducible, so that an amperometric titration curve at this potential will be V-shaped. The soln. is de-oxygenated with N for 10 min. before titration. After each addition of titrant, N is again passed, and the ppt. is then allowed to settle for 1 min., before reading the current. For 11 titrations of Co^{2+} soln. (0·1 to 10 mM), the mean error was ±0·16%. The results confirm that the ppt. is $CoTeO_3$.
G. RUSSELL

4655. **Chromatographic recovery of the nitroso-complex of cobalt.** A. Kh. Sult. Publ.: "Khromatografiya, ee Teoriya i Primenenie," Akad. Nauk SSSR, Moscow, 1960, 445–449; *Ref. Zhur., Khim.*, 1961, (5), Abstr. No. 5D90.—The complex of Co with nitroso-R salt (**I**) must be separated from the excess of **I**, which interferes with the photometric determination. *Procedure*—To the test soln. (15 ml) add citrate buffer mixture until the soln. is slightly alkaline, and 0·5% **I** soln. (2 ml), heat the mixture on a boiling-water bath for 20 to 30 min., add HNO_3 (1:1) until the colour changes to orange and heat for another 5 min. to convert Fe, Ni and Cu into the cationic forms which are not adsorbed by alumina. Pass the mixture at 3 ml per min. through a column (diam. 12 mm) containing a 2-cm layer of alumina. Wash the column with H_2O, elute **I** with N-HNO_3 at 80° or, better, 0·25N-$NaNO_3$ at 80°. Elute the Co complex with 0·2N-H_2SO_4. Dilute the eluate to 10 ml with H_2SO_4 soln. and measure it photometrically with a green filter.
K. R. COOK

4656. **Polarographic determination of cobalt by the use of EDTA.** Genkichi Nakagawa and Tsuyoshi Nomura (Nagoya Inst. Tech., Gokiso-cho, Showa-ku, Nagoya). *Japan Analyst*, 1960, **9** (2), 91–95.—The Souchay and Faucherre method in which the reduction wave of Co^{III} - EDTA is used (*Anal. Chim. Acta*, 1949, **3**, 252) was examined. The wave height is constant at pH 8 to 9 in the presence of 0·03M to 0·06M-EDTA (disodium salt) in a borate buffer and is proportional to the concn. for <0·004M. The oxidation of Co with PbO_2 at pH 9 is complete within 15 min. There is no interference from Ni, Zn (<120 mg per 100 ml), Cu, Pb or V; Mn, Fe and Cr interfere.

K. SAITO

4657. **Determination of cobalt in nickel by surface treatment.** G. V. Loshkareva. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 146–149; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D113.—This method is based on the stability of the complex of Co with nitroso-R salt (**I**) in HNO_3 medium, while the corresponding nickel and copper compounds are decomposed. Place 3 drops of aqua regia in cavities in the standard and test samples. After 10 min. transfer the soln. to test-tubes, wash out the cavities with 2 drops of water (3 or 4 times), boil the resulting soln. and wash liquors to remove oxides of N, cool, add to each soln. 20 drops of 0·5% aq. **I** soln. and 14 drops of 40% Na acetate soln., boil for 1 to 2 min., add 1·0 to 1·5 ml of conc. HNO_3, again boil for a few minutes, cool and make up to 10 ml. For the colorimetric determination of Co, a visual comparison can be made or the extinction is measured, with a blue filter. Comparison of the surface-treatment and potentiometric methods for the determination of Co in types N3 and N4 nickel shows that the former method is satisfactorily accurate. The determination takes ≃25 min.

C. D. KOPKIN

4658. **Micro-determination of traces of cobalt in cement by spectrophotometry.** W. Haerdi, J. Vogel and D. Monnier (Lab. de Chim. Min., de Chim. Anal. et de Microchim., Univ., Genève, Switzerland). *Anal. Chim. Acta*, 1961, **24** (4), 365–370 (in French).—The determination is important because Co present in the cement used in atomic reactors may acquire undesirable radioactivity. *Procedure*—Dissolve the sample (0·05 to 0·5 g) in conc. HCl (10 ml), add a few drops of conc. HNO_3 and evaporate on a boiling-water bath to 3 ml. Add 9M-HCl (10 ml), cool, centrifuge and transfer the supernatant liquid to a Dowex 1-X8 column. Elute Co from the column with 4M-HCl. To the eluate add 5% NaCl soln. (0·5 ml) and evaporate to dryness. Dissolve the residue in water (2 ml), add 2 ml of an acetic acid - Na acetate buffer (pH 6), add 0·05% nitroso-R salt soln. (0·5 ml) and heat in a boiling-water bath for 1 min. Add conc. HNO_3 (0·5 ml), heat for 30 sec., cool, dilute to 5 ml, centrifuge and measure the colour at 520 mμ. Loss of Co during the procedure was calculated by comparing the radioactivity of ^{60}Co added to the sample with that remaining in the final soln., and was found to be <10%. The amounts of Co in the cements examined varied between 0·0004 and 0·0010%, with an error <±6%. The Co remaining in the insoluble residue was <3%.

A. J. BENNETT

4659. **New method for the determination of small amounts of cobalt in the presence of iron.** L. T. Ikramov. *Trudy Tashkent. Farmatsevt. Inst.*, 1960, **2**, 341–344; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D137.—The extraction of the cupferron complexes of Co and Fe with $CHCl_3$ at various pH values is studied, and a colorimetric method is developed for the determination of Co with nitroso-R salt after extraction of Fe as the cupferron complex at pH <1. *Procedure*—Evaporate the sample to dryness, add HCl to the dry residue to a concn. ≃M (vol. of soln. 10 to 15 ml), add 7 ml of a 6% soln. of cupferron (**I**), mix and shake with 10 ml of $CHCl_3$; repeat the extraction with 3 ml of **I** soln. and 5 to 7 ml of $CHCl_3$, repeating till the org. layer is colourless. Evaporate the aq. layer to dryness on a water bath, destroy the excess of **I** by heating with a mixture of HNO_3 and H_2O_2 (3:1), add to the dry residue 10 ml of mixed acids (10 ml of conc. HCl and 100 ml of conc. HNO_3 diluted to 400 ml), heat to boiling and add 7 ml of reagent soln. (mix 20 ml of 0·1% nitroso-R salt soln. and 50 ml of a 50% soln. of cryst. Na acetate), boil for 1 min., add 3 ml of conc. HNO_3, again boil for 1 min., make up to 25 ml and measure the extinction. The relative error is 2 to 5% at a ratio of Co to Fe of 1:5000.

C. D. KOPKIN

4660. **Studies on chemical analysis by the use of organic reagents. IV. Photometric determination of nickel with 1,2-di-(o-aminobenzylideneaminoethane.** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *Japan Analyst*, 1960, **9** (4), 269–271.—1,2-Di-(*o*-aminobenzylideneamino)ethane produces a red ppt. with Ni at pH >9·6. This ppt. is sol. in benzene and can be extracted from aq. soln. The benzene soln. has an absorption max. at 486 mμ and Beer's law is obeyed for <9 μg of Ni per ml. Manganese, Al, Cr, Pb, Sn, Sb, Cd, Ca, Ba and Mg (<50 mg each) and Co (<10 times the wt. of the Ni) do not interfere in the presence of tartrate.

K. SAITO

4661. **The colorimetric micro-determination of nickel as methyltriphenylarsonium bis[dithio-oxalato]nickelate(II).** A. J. Cameron and N. A. Gibson (Chem. School, Univ., Sydney, N.S.W., Australia). *Anal. Chim. Acta*, 1961, **24** (4), 360–364 (in English).—Place a soln. (<25 ml) containing 25 to 250 mg of Ni in a separating-funnel. Make the soln. acid to Congo red paper and then add 10% Na acetate soln. (3 to 5 ml in excess of that required to turn the indicator red). Add the extracting solvent (acetophenone - $CHCl_3$) (11:9) (5 ml), 0·25% K dithio-oxalate soln. (2 ml) and 0·5% methyltriphenylarsonium chloride soln. (2 ml). After extraction, filter the organic layer through sintered glass and extract the aq. layer twice with 5-ml portions of the extracting solvent. Make the filtrate and washings up to 25 ml and compare with a blank soln. in a Spekker absorptiometer using heat absorption filter H503 and green spectrum filter 604. The mean error is <1%. Iron, Cu and Co interfere, and a method is suggested for their removal by extraction of the thiocyanates with $CHCl_3$.

A. J. BENNETT

4662. **New selective micro-methods in the analysis of metals. Titrimetric determination of small amounts of nickel at an equivalent ratio of 1:24.** K. Burger (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Talanta*, 1961, **8** (4), 253–256 (in English).—Use is made of the great selectivity of the nickel dimethylglyoxime gravimetric method to determine amounts of Ni in the range 75 to 250 μg. Nickel is pptd. from ammoniacal soln. by dimethylglyoxime. The ppt. is dissolved in HCl soln. and hydrolysed to produce

an equiv. amount of hydroxylamine, which is then oxidised to HNO_3 by an excess of standard BrCl soln.; KI is added to the final reaction mixture and the liberated iodine is titrated with $Na_2S_2O_3$. An error of the order of $\pm 1\%$ can be expected.

G. S. ROBERTS

4663. **Volumetric determination of metals via precipitation with organic reagents. Permanganometric determination of nickel precipitated by dimethylglyoxime.** K. Bhaskara Rao (Dept. of Mines and Tech. Surveys, Ottawa, Canada). *Z. anal. Chem.*, 1961, **180** (4), 271–275 (in English).—The ppt. of Ni dimethylglyoxime is dissolved in hot HCl (1:1) (15 to 20 ml), diluted to 90 to 100 ml, then hydrolysed to hydroxylamine by boiling for 15 to 20 min., and diluted to $\simeq 250$ ml; the soln. is then heated to 55° to 60°, 2 ml of M-$CuCl_2$ is added and the hydroxylamine is determined by titration with 0·1N-$KMnO_4$. For amounts of Ni from 0·5 to 2·3 mg the error is $< 1{\cdot}3\%$. T. R. ANDREW

4664. **Phase analysis of nickel-base alloys.** Yu. A. Klyachko and M. M. Shapiro. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 383–392; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D186.—A method is developed for the phase analysis of stainless nickel-base alloys, comprising the separation of the phases by electrolysis with an anode current density of 0·025 amp. per sq. cm at 7° to 9°, using as electrolyte a soln. containing $FeSO_4 \cdot 7H_2O$ 3, NaCl 3·5, and H_2SO_4 5%. Under these conditions there is complete separation of the intermetallide phase (*A*). The *A* and carbides are determined in a single sample. After the electrolysis the ppt. is separated from the sample, washed with water and ethanol, dried, and analysed by electron microscopy and by X-ray structural analysis. The *A* is separated from the carbide phase by treating the water-washed ppt. with 10% H_2SO_4, first in the cold and then by heating for 30 min. to 90°; the *A* dissolves, and the soln. is analysed by usual methods. The insol. residue is analysed for its carbide content by electron microscopy and X-ray structural analysis. The carbides are determined by transferring the residue, washed with water, to a funnel with freshly ignited asbestos, drying in a stream of H, and determining C by ignition at 1300°. To determine non-metallic inclusions, a separate sample is leached for 24 hr., and the residue treated with acid oxidising mixtures by the standard method for the analysis of non-metallic inclusions in steel. C. D. KOPKIN

4665. **Photometric determination of nickel in copper alloys without removal of copper.** I. I. Kalinichenko and A. A. Kinyazeva. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (3), 418–421; *Ref. Zhur., Khim.*, (6), 1961, Abstr. No. 6D138.—In the colorimetric determination of Ni in copper alloys (3·5 to 5·0% of Ni) with dimethylglyoxime (**I**) in the presence of oxidising agents, the interference due to Cu is overcome by the addition of EDTA (disodium salt) (**II**). The dark-green dimethylglyoxime complex of Cu is not completely destroyed by **II** in alkaline medium, but is completely destroyed in ammoniacal medium. The method gives reliable results with a ratio of Ni to Cu of $< 1:40$. *Procedure*—Dissolve the sample (0·1 g) in 5 to 6 ml of HNO_3 (1:3), boil to remove oxides of N and make up to 250 ml. To 10 ml of the resulting soln. add 2 ml of 10% K Na tartrate soln., 5 ml of fresh 10% $(NH_4)_2S_2O_8$ soln., 5 ml of 4% NaOH soln. and 5 ml of a 1% soln. of **I** in 4% NaOH and mix. After 3 to 5 min., add 5 ml of 0·1N-**II** and 5 ml of 5% NH_4Cl soln., make up to 100 ml and measure the extinction in a 1-cm cell. For comparison soln. use 10 ml of sample soln. treated as described above, but with NaOH instead of **I**. The discrepancy between the results and those of the gravimetric determination of Ni is 0·3 to 2·5%. The determination takes 30 to 35 min. C. D. KOPKIN

4666. **Analysis of zinc eluates and electrolytes. Determination of small amounts of nickel.** Z. Hašek (Res. Inst. of Metals, Panenské Břežany, Czechoslovakia). *Hutn. Listy*, 1961, **16** (4), 281–282.—After reaction with dimethylglyoxime, Ni is extracted into $CHCl_3$ and determined colorimetrically. *Procedure*—Make the sample (10 to 15 ml) slightly acid with dil. H_2SO_4 and oxidise Fe^{2+} with 0·1N-$KMnO_4$. Add Na tartrate soln. (5%) (10 ml) and adjust to pH 4·0 with NaOH soln. Add $Na_2S_2O_3$ soln. (40%) (10 ml) for masking Cu, acetate buffer soln. (pH 6) and hydroxyammonium chloride (50 mg). Adjust the pH to 5·2 to 5·3, dilute the soln. with H_2O to 50 ml, add dimethylglyoxime soln. (1%) (2 ml) and shake for 1 min. Add $CHCl_3$ (6 ml) and shake again for 1 min. Filter the $CHCl_3$ extract through paper and measure the extinction at 380 mμ. Compare with a calibration curve. The method takes 5 to 10 min.

J. ZÝKA

4667. **Spectrophotometric determination of micro amounts of nickel in uranium with dimethylglyoxime.** Kenji Motojima, Hiroshi Hashitani and Kazuo Katsuyama (Japan Atomic Energy Res. Inst., Tokyo). *J. Atomic Energy Soc., Japan*, 1961, **3**, 89–92 (in Japanese).—A spectrophotometric method is critically examined. Nickel is determined spectrophotometrically after extracting its dimethylglyoxime complex with $CHCl_3$. Approx. 30 ml of acid soln. containing not more than 2·5 g of U and 150 μg of Ni is treated with 10 ml of 30% ammonium citrate soln., 1 ml of dimethylglyoxime soln. (1 g in 100 ml of 95% ethanol), and aq. NH_3 to adjust the pH to 8·8 to 10, and the vol. is brought to 50 ml. Then the nickel complex is extracted with exactly 10 ml of $CHCl_3$, and the extinction of the extract is measured at 375 mμ, with a blank as reference. By this method, as little as 5 μg of Ni in 2·5 g of uranium can be determined rapidly and accurately. The method provides for the presence of other metals. NUCL. SCI. ABSTR.

4668. **Determination of copper in nickel by surface treatment.** G. V. Loshkareva. *Trudy Ural'sk. Politekh. Inst.*, 1960, (96), 150–155; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D69.—Guaiacol (**I**) is used as reagent. Paraffin-wax cells of diam. 8 to 10 mm are constructed on the surface of a standard and the test samples of nickel; the bottoms of the cells are dissolved out with ethanol, and the surface of the metal is etched with 3 or 4 drops of aqua regia, washed with water and dried with filter-paper. Three drops of aqua regia are placed in the cells, and after 10 min. the soln. are transferred to small tubes, the cells are washed with water (2 drops) three or four times, the soln. and wash liquors are boiled to remove oxides of N, then cooled, and made up to 10 ml. Conc. aq. NH_3 (25 drops) and 3% H_2O_2 soln. (6 drops) are added to 0·5 or 1 ml of test and standard soln., and the soln. are heated till no more NH_3 is given off. The soln. are cooled, 10 drops of conc. aq. NH_3 are added, and the soln. are made up to 100 ml. To 0·5- or

1-ml aliquots are added 15 drops of 1% **I** soln. and 1 or 2 drops of H_2SO_4 (1:20), and the colours are compared visually, after 5 min., or the extinctions are measured, with a blue filter. Comparison of the titrimetric and the surface-treatment methods has shown that the latter method is satisfactorily accurate. The determination takes 35 min.

C. D. KOPKIN

4669. Determination of ruthenium tetroxide. C. J. Anderson, R. Del Grosso and M. H. Ortner (Cross-Malaker Lab., Mountainside, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 646–647.—This method was developed in a study of the kinetics of the decomposition of RuO_4 in sealed Carius tubes, which contained, in addition to RuO_4, such materials as RuO_3 and ruthenium metal, with or without silica gel and $MgClO_4$. The sample is extracted with CCl_4, and the extract is added to 2N-KOH and heated at 70° to 75° until the CCl_4 layer is clear. The aq. layer is removed and diluted to a known vol. with 2N-KOH, and the extinction of the soln. is measured at 465 mμ. Recoveries on ≃ 50 mg of RuO_4 range from 96 to 100%.

T. R. ANDREW

4670. Photometric determination of palladium with furil α-dioxime. V. M. Peshkova, V. I. Shlenskaya and S. S. Sokolov. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **11**, 328–338; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D105.—Small amounts of Pd are determined by means of furil α-dioxime (**I**) in non-aq. soln. To the slightly acid soln. of a Pd salt (pH 3·0 to 4·0) is added 5 parts of 0·2% ethanolic **I** soln., the mixture is stirred for 2 to 3 sec. to coagulate the ppt. and then extracted with benzene (2 × 5 ml). The organic soln. is freed from traces of moisture, and the extinction is measured in a colorimeter at 436 mμ or in a spectrophotometer at 297 mμ. Nickel, Co, Cu, Ir, Ru, Pt and Rh do not interfere, but Fe^{III} does. Binding the Fe as a phosphate complex gives satisfactory results at ratios of Pd to Fe of <1:100. The interference of Au (at ratios of Pd to Au of <1:30) is avoided by adding a soln. of hydroxyammonium chloride. Errors in the determination of Pd in the presence of 1000-fold amounts of Ni^{2+}, Co^{2+}, Cu^{2+}, Pt^{4+}, Ir^{4+}, Rh^{4+} and Ru^{4+}, and 10 to 20-fold amounts of Fe^{3+} and Au^{3+}, are ±5%.

A. BURWOOD-SMITH

4671. Spectrophotometric determination of palladium with nitrilotriacetic acid. P. G. Desideri and F. Pantani (Inst. of Anal. Chem., Univ. Florence, Italy). *Talanta*, 1961, **8** (4), 235–240 (in English).—The formation of the Pd - nitrilotriacetic acid complex is described. A stable soln. of const. extinction at 330 mμ is obtained in the pH range 3 to 11. An excess of reagent produces a bi-co-ordinated complex. Other metals of the Pt group interfere when present in appreciable amounts, but this can be avoided by first separating the Pd with dimethylglyoxime (Ayres and Berg, *Anal. Chem.*, 1953, **25**, 980).

G. S. ROBERTS

4672. X-ray-fluorescence spectral analysis of geochemical samples for elements of atomic numbers 25 to 40. K. H. Wedepohl (Mineralog.-Petrograph. Inst., Univ., Göttingen). *Z. anal. Chem.*, 1961, **180** (4), 246–259 (in German).—A Philips X-ray fluorescence spectrograph with vacuum attachment, a tungsten anode, a lithium fluoride analysing crystal and a thallium-activated sodium iodide scintillation crystal detector is used. Iron, Ni, Cu and Zn are determined with added As as an internal standard, while Mo is used as the standard for Br, Rb, Sr, Y and Zr. The relative error in the range 0·01 to 0·1% is 3 to 5%. For the determination of Fe (up to 10%), a relative error of 2·5% is reported.

T. R. ANDREW

4673. Procedure for the analysis of uraninite [pitchblende]. I. A. Tserkovnitskaya and A. K. Charỹkov. *Uch. Zap. Leningrad. Gos. Univ.*, 1960, (297), 109–118; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D133.—A rapid method is given for the determination, on a single sample, of SiO_2, total U, Pb, Th, total rare-earth elements, CaO and MgO, based on the separation of the major elements by extraction followed by complexometric titration.

A. BURWOOD-SMITH

4674. Determination of minor constituents in pyrrhotite with ion-exchange resin. Yoshimi Umezaki (Resources Res. Inst., Kotobuki-cho, Kawaguchi, Saitama-ken). *Japan Analyst*, 1960, **9** (2), 138–143.—After the removal of Fe from HCl soln. by extraction with ether, Cu, Co and Zn are separated by the Kraus and Moore method (*J. Amer. Chem. Soc.*, 1953, **75**, 1460) from Ca, Mg, Al, Ti, Mn and Ni, which are not adsorbed on the anion-exchange resin. Cobalt, Ti, Mn and Ni are determined photometrically, and Ca, Mg, Al and Zn by EDTA titration. *Procedure*—Dissolve the sample (1 g) in conc. HCl (20 ml), add HNO_3 (5 ml), boil with HCl, dilute and filter. Treat the ignited residue with HF and determine the Si. Make up the filtrate to 50 ml (HCl concn., 6N), shake with ether (50 ml) and evaporate the aq. layer almost to dryness. Dissolve the residue in 7N-HCl (10 ml), and pass the soln. through a column (diam. 1·1 cm, length 11 cm) of Dowex 1-X8 (100 to 200 mesh) at 1 ml per min., then wash the resin with 7N-HCl (40 ml). Precipitate Al and Ti in the eluate with aq. NH_3 and titrate the sum of Mg and Ca, by the usual EDTA method in the presence of KCN. Titrate Al in the ppt. with EDTA [Cu complex of 1-(2-pyridylazo)-2-naphthol as indicator] and determine the Ti with H_2O_2. Determine Mn photometrically in another aliquot of the eluate by the KIO_4 method, and Ni by the dimethylglyoxime method in the presence of Br and citric acid. Elute the resin column with 5N-HCl (90 ml) at 2 ml per min. and then with 2N-HCl (50 ml) to remove the remaining Fe. Titrate the sum of Cu and Co in the 5N-HCl soln. with EDTA (to murexide) and determine the Co with nitroso-R salt. Finally elute the column with 0·5N-HNO_3 (80 ml) and titrate Zn with EDTA (to Eriochrome black T).

K. SAITO

4675. A rapid method for the analysis of smaltite concentrates. I. J. Robin, P. Dewasnes and P. Dévoré (Soc. d'Électrochim., Ugine, Lab. des Serv. Centr. de Rech., Lyon, France). *Bull. Soc. Chim. France*, 1961, (2), 223–225.—The sample (1 g of crude or 0·5 g of roasted concentrate) is dried at 110° and dissolved in HCl (*d* 1·19) (10 ml) and HNO_3 (*d* 1·33) (10 ml) (requiring 0·5 hr. in the cold or on slight warming). Silica is rendered insol. by adding $HClO_4$ (*d* 1·6) (10 ml) and evaporating to white fumes and a vol. of 2 to 3 ml. The SiO_2 separated from the crude concentrate is white and pure, but from the roasted concentrate it is coloured and must be determined by volatilisation with HF, and the residue from the volatilisation must be dissolved in HCl and added to the filtrate. The filtrate is diluted to between 250 and 300 ml (to an acid

concn. of <0·3N) and passed through a cation exchanger at 7 ml per min. (12 ml of resin in a tube of cross-section 1 sq. cm). The percolate and washings with water (200 ml) are made up to 500 ml and the AsO_4^{3-} are determined iodimetrically (any Cr is determined with diphenylcarbazide and corrected for). The cations adsorbed are eluted with 2N-HCl (500 ml at 7 ml per min., or 150 ml at 2 ml per min.), and the Fe is determined volumetrically with $K_2Cr_2O_7$ after reduction with $SnCl_2$, the Co by potentiometric titration with $[Fe(CN)_6]^{3-}$ (including a correction for any Mn present), and the Ni gravimetrically with dimethylglyoxime. Alternative methods are discussed in which the Fe is eluted from the column first with oxalate. The Co and Ni can be determined together by electro-deposition and the Ni determined separately after dissolution of the deposit. The titrimetric determination of Co is preferred.

II. Use of cobalt-60 as a tracer. J. Robin, P. Lebreton and P. Dévoré. *Ibid.*, 1961, (2), 225–228.—The completeness of operations in the analysis of smaltite by the method of Robin *et al.* (Part I) is tested by the addition of 3 μC of ^{60}Co to the original soln. of ore. The recovery is monitored discontinuously or, by means of an integrating device, continuously on the percolate of the cation exchanger. It is shown that the SiO_2 residue from a crude ore retains <0·1% of Co, but that from a roasted ore retains an appreciable amount of Co, so that the residue from the HF volatilisation of the SiO_2 must be added to the filtrate. The arsenical eluate contains a negligible quantity of Co if the acid concn. is <0·3N and the rate of flow is ≃7 ml per min. For a total elution of cations with 2N-HCl all the Co is eluted from the column before all the Fe has come off. When Fe is eluted first by means of oxalic acid, the Co remains on the column, but is completely eluted with 150 ml of 2N-HCl. The effect of acidity and rate of elution on the elution of Co is studied and the optimum conditions are established.

E. J. H. Birch

4676. **Determination of oxide-film thickness by proton activation.** B. A. Thompson (Gen. Engng Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 583–586.—The method described, based on the activation of naturally occurring ^{18}O with protons, according to the reaction $^{18}O(p,n)^{18}F$, has been successfully applied to the measurement of oxide-film thickness on tantalum. The lower limit of detection corresponds to a thickness of the order of 1 A, the upper limit is approximately 10^5 A. Elements interfering are Cu, Ni, Zn and Ti; the interference from Ti is avoided by using proton energy below 3·8 meV. The method is equally applicable to the determination of the oxygen content of almost any type of thin film and, with proper standardisation, to the determination of trace amounts of O in metals.

C. B. Baines

4677. **Spectral solution analysis of slags.** H. Jelínek (Res. Inst. for Iron Metallurgy, Prague). *Hutn. Listy*, 1961, **16** (4), 276–279.—*Preparation of the sample*: (*i*) *for homogeneous samples*—Fuse the sample (0·1 g) in a platinum crucible with a ten-fold excess of Na_2CO_3 - K_2CO_3 - $Na_2B_4O_7.10\,H_2O$ (3:3:4), dissolve the melt in aq. HCl - citric acid (500 ml of conc. HCl and 35 g of citric acid in 1 litre of H_2O) (14 ml) at 50°, add $CoCl_2$ soln. (1 ml ≡20 mg of Co) (10 ml) as internal standard and dilute with H_2O to 50 ml. (*ii*) *For non-homogeneous samples*—Fuse the sample (0·5 g) as described above, dissolve the melt in 70 ml of aq. HCl - citric acid and dilute to 200 ml. Add $CoCl_2$ soln. to a 40-ml aliquot for spectrographic analysis. The content of the following elements was determined—Si, Fe, Mn, Al, Ca, Mg, Cr, Ti and V.

J. Zýka

See also Abstracts—**4446**, Dithiocarbamate as reagent for Cu. **4449**, Phosphorodithioates as reagents for metals. **4452**, Micro-analysis by radiometric pptn. **4454**, Indicator for EDTA titrations. **4456**, Amperometric titrations with ICl. **4701**, Determination of hydrazine. **4723**, V in petroleum oils. **4724**, Ni and V in petroleum distillates. **4854**, ^{137}Cs, ^{90}Sr and ^{140}Ba in rain-water. **4855**, Ra in water. **4858**, Cu by atomic absorption spectrophotometry. **4868**, Thermal-conductivity gas analysis for He - CO_2. **4869**, Manometric determination of oxides of N. **4870**, Gases in metals. **4904**, Ca, Mg and Zn in sand. **4905**, Photometric determination of elements.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather and explosives.

4678. **Specific tritium-labelling by heterogeneous exchange on gas-chromatography columns.** G. Stöcklin, F. Schmidt-Bleek, and W. Herr (Inst. f. Nucl. Chem., Univ., Cologne, Germany). *Angew. Chem.*, 1961, **73** (6), 220.—The exchange reaction at 100° to 200° of an alkyl halide, carried by an inert gas into Ca^3H_2 (prep. given) and then into a gas-chromatographic column permits isolation of specifically labelled substances free from unchanged halide and tritium gas. The method is particularly useful for the prep. of volatile hydrocarbons, *e.g.*, [1-^{3}H]pentane and [α-^{3}H]toluene (from n-amyl and benzyl bromides, respectively) with high specific ^{3}H activity.

J. P. Stern

4679. **The selective determination of active hydrogen with dispersed sodium.** P. R. Mohilner and C. A. Reynolds (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Talanta*, 1961, **8** (4), 223–227 (in English).—Compounds containing active hydrogen are classified according to their reactivity, *viz*, as the most reactive (acids, alcohols and some phenols), the less reactive (acetylated amines, sulphonamides and some phenols), and the least reactive (aldehydes, ketones, amines, esters and 1-acetylenes). Three methods of analysis are given for the assignment of a compound to one of these classes—(*i*) a conventional method which will determine the active hydrogen in any of the compounds listed, *e.g.*, the Zerewitinoff or the $LiAlH_4$ method; (*ii*) the method of Mohilner and Reynolds (*Trans. Kans. Acad. Sci.*, 1960, **63**, 72) in which the most reactive class of compounds can be determined by adding an excess of a standard dispersion of Na in xylene - dioxan (1:2) to a soln. of the compound in xylene, converting the excess of Na into Na ethoxide which is then titrated with standard acetic acid soln.; the wt. of Na which reacted with the

compound can then be calculated; and (*iii*) the method here described, in which the pressure change in a constant-vol. system, caused by the H evolved on treating the compound with dispersed Na, is measured. Compounds in the two most reactive classes can be determined by this method.
G. S. ROBERTS

4680. **Determination of chlorine and bromine in liquid organic compounds by the Schöniger - Bennewitz micro-method.** I. A. Favorskaya and V. I. Lukina. *Vestn. Leningr. Univ.*, 1961, No. 10, *Ser. Fiz. i Khim.*, (2), 148–151.—Solid and liquid organic halogen compounds can be analysed for halogen, S and P contents by burning the compound in a Schöniger flask. Although the Bennewitz - Schöniger method (Bennewitz, *Anal. Abstr.*, 1960, **7**, 3784) gives good results with liquid halogen compounds it is unsuitable for high halogen contents. It is suggested that compounds should be burnt on a filter-paper saturated with 2% KNO_3 soln., which ensures the complete combustion of compounds such as trichloroethylene, dibromoethane, and 1,3-dibromopropane. The final determination of Cl and Br is by titration with 0·01N- or 0·02N-$Hg(NO_3)_2$, with diphenylcarbazone as indicator.
A. BURWOOD-SMITH

4681. **Photometric determination of organic nitrogen by Kjeldahl method without distillation.** Motomu Kasagi and Masayuki Ito (Chem. Dept., Defence Academy, Yokosuka). *Japan Analyst*, 1960, **9** (2), 105–109.—The photometric method of Kruse and Mellon (*Anal. Abstr.*, 1954, **1**, 276) was applied to ammonium sulphate soln. obtained by the Kjeldahl method. To avoid interference from the digestion catalyst, the coloured product is extracted with CCl_4. The time taken for an estimation is ≃35 min. *Procedure*—Heat the sample (<10 mg) with conc. H_2SO_4 (4 ml) and K_2SO_4 (2 g) [or $HgSO_4$ (0·5 g) and K_2SO_4 (1·5 g)] for 20 min. Make up the product to 1 litre and adjust a 20-ml portion with Na acetate (0·4M) to pH 2·8. Add chloramine-T soln. (3%) (1 ml), set aside for 90 sec. and add pyrazolone reagent [a mixture of 25 ml of aq. 0·2% 3-methyl-1-phenyl-5-pyrazolone and 4 ml of 0·1% bi-(3-methyl-1-phenyl-5-pyrazolonyl) in pyridine], shake with CCl_4 (20 ml) after 1 min. and measure the extinction at 460 mμ.
K. SAITO

4682. **Determination of nitrogen in organic compounds without distillation. I.** M. Ashraf, M. K. Bhatty and R. A. Shah (Dept. Pharm., Punjab Univ., Lahore). *Pakistan J. Sci. Ind. Res.*, 1960, **3** (1), 1–3.—The compound (0·1 to 0·2 g) is mixed with 5 g of K_2SO_4 and 0·6 g of $HgSO_4$ and digested with 8 ml of conc. H_2SO_4, for 45 min. if the N is situated in an open chain, or for 1·5 hr. if it is in a ring. The cooled digest is washed into a conical flask, treated dropwise, with shaking, with NaOH soln. till a yellow ppt. of HgO is produced, then cooled and neutralised with $NaHCO_3$; 4 g of KBr is then added and the mixture is shaken until a clear soln. is obtained. An excess of 0·2N-NaOCl is then added until the soln. becomes pale yellow, followed, after 5 min., by a known excess of 0·1N-arsenous oxide, the excess of which is back-titrated with the NaOCl soln., with 0·2% aq. Bordeaux B as indicator; 1 ml of 0·2N-NaOCl ≡ 0·934 mg of N. Results for 13 compounds agreed well with the theoretical values. Nitro-compounds containing <10% of nitro-N can be determined by this method without pre-reduction.
R. E. E.

4683. **Sub-micro methods for the analysis of organic compounds. XI. Determination of tertiary nitrogen by use of an ion-exchange resin.** R. Belcher, M. K. Bhatty and T. S. West (Univ., Birmingham, England). *J. Chem. Soc.*, 1960, 2473–2475.—The compound is treated with methyl iodide to form the corresponding quaternary ammonium iodide; this is dissolved in water and converted into its hydroxide by passage through a column of Amberlite IRA-400 (OH^- form). The eluate is titrated with 0·01N-H_2SO_4 to a methyl red - methylene blue indicator. While the method is not applicable to compounds that do not react quant. with methyl iodide it has been used for the analysis of several alkaloids, with an accuracy within 0·3%.
N. E.

4684. **Micro-determination of sulphur in organic compounds.** Takero Sudo, Daizo Shimoe and Takatomo Tsujii (Kurosaki Factory, Mitsubishi Chem. Ind., Yawata, Fukuoka-ken). *Japan Analyst*, 1960, **9** (2), 109–112.—The oxidation of SO_2 is facilitated by the use of a platinum catalyst at 400° to 500°. The absorption by electrolytic silver (1 g) (Mitsui and Sato, *Anal. Abstr.*, 1957, **4**, 917) is quant. at 390° to 410°. The error is <0·2% (absolute) for various compounds containing <25% of S.
K. SAITO

4685. **Fusion of organic substances with magnesium. IX. Micro-determination of silicon in organic compounds.** J. Jeník and M. Jureček (Inst. for Anal. Chem., Tech. Coll. Chem., Pardubice, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1961, **26** (4), 967–973 (in German).—Magnesium silicide formed on fusion with magnesium is decomposed with dilute H_2SO_4 and the gaseous silicon hydrides formed are absorbed in bromine water and thus hydrolysed to silicic acid. The silicic acid is converted into molybdosilicic acid and determined colorimetrically as molybdenum blue. The error is +0·73 to −0·54% over the range 10·53 to 37·8% of Si. Halogens can be determined on the same sample; after removal of silicon hydrides, the elementary carbon which separates is de-activated with ferric or aluminium salts and filtered off, and halogens are determined in the filtrate by Volhard's method.
R. PRESSER

4686. **Continuous infra-red functional-group detection of gas-chromatographic eluates.** E. A. Haahti and H. M. Fales (Nat. Heart Inst., Educ. and Welfare, Bethesda, Md., U.S.A.). *Chem. & Ind.*, 1961, (16), 507–508.—The hot eluate gas stream is passed into a circulating solution cell. The infra-red spectrograph is adjusted to the desired frequency and the chart-drive adjusted to match that of a thermal-conductivity detector, also in the gas stream. The sensitivity of the apparatus is high for substances containing carbonyl or methylene groups.
C. B. BAINES

4687. **Applications of infra-red spectroscopy. IV. The causes of anomalous alkoxyl determinations given by sugars and polyhydric alcohols.** D. M. W. Anderson and J. L. Duncan (Dept. of Chem., Univ., Edinburgh). *Talanta*, 1961, **8** (4), 241–248 (in English).—The causes of errors are discussed and recommendations for their avoidance are made. High results can be produced by iodine vapour passing aq. scrubbers, but this effect can be eliminated by the use of soda asbestos scrubbers. Sample wt. should not exceed the minimum

required to produce a determinable quantity of methyl iodide, and reflux times should probably not exceed 12 min. One of the products of reaction has been identified as 2,5-dimethylfuran, which is not absorbed by either aq. or soda asbestos scrubbers and which behaves like methyl iodide during the thiosulphate titration. Polysaccharides tenaciously retain small amounts of organic solvents used in their preparation, and the use of solvents containing alkoxyl groups should if possible be avoided. G. S. ROBERTS

4688. **Detection of olefins by epoxidation and hydroxamation and characterisation by rearrangement of epoxides to carbonyl compounds.** J. G. Sharefkin and H. E. Shwerz (Brooklyn College, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 635–639.—Commercial 40% peroxyacetic acid converts olefins, on heating or in acid medium, into their glycol monoacetates; these are treated with hydroxylamine and the hydroxamic acids produced are detected as the wine-red ferric salts. Olefins are also characterised by their conversion, with peroxyacetic acid, under mild or alkaline conditions, into epoxides, which, on addition of boron trifluoride - ethyl ether, undergo isomerisation to carbonyl compounds, which are then converted into their solid dinitrodiphenylhydrazones. These are identified from their m.p. and u.v. spectra. G. P. COOK

4689. **Detection and characterisation of acetylenes by hydration to carbonyl compounds and formation of 2,4-dinitrophenylhydrazones.** J. G. Sharefkin and E. M. Boghosian (Brooklyn Coll., N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 640–644.—Acetylenes are hydrated with a BF_3 - HgO - trichloroacetic acid catalyst. The resulting carbonyl compounds are treated with 2,4-diphenylhydrazine and the formation of a phenylhydrazone is confirmed by addition of methanolic KOH to produce a wine-red colour. The test also permits the detection of the acetylene in the presence of an olefin bond in either the same molecule or in mixtures. G. P. COOK

4690. **Polarographic study of divinylacetylene and aldehydes in dimethylformamide.** Shiro Usami (Kurashiki Rayon Co., Toyama). *Japan Analyst*, 1960, **9** (3), 216–220.—In dimethylformamide (**I**) containing tetrabutylammonium iodide, divinylacetylene (**II**) gives a two-step wave at −1·74 and −2·22 V *vs.* the S.C.E. Crotonaldehyde and acraldehyde give one-step waves at −1·48 and −1·29 V, respectively. Saturated aldehydes give a one-step wave at −2·25 V. The first wave of **II** and the waves of unsaturated aldehydes are not affected by vinyl acetate (**III**) (<75%) in **I**, whereas the waves of saturated aldehydes are covered by that of **III**. In the presence of water in **I** and **III**, the wave of acetaldehyde is shifted to −1·89 V. K. SAITO

4691. **Influence of sulphuric acid concentration on the determination of methanol by the Widmark method.** R. Dynakowski and J. Kubalski (Dept. of Forensic Med., Med. Acad., Warsaw, Poland). *Acta Polon. Pharm.*, 1961, **18** (1), 21–24.—The low results obtained in the Widmark method for concn. of methanol >2 p.p.m. are due to the decomposition of formic acid by the conc. H_2SO_4 and liberation of CO. This error is eliminated, even for concn. up to 5 p.p.m. of methanol, if H_2SO_4 diluted with H_2O (1:1, v/v) is used instead of conc. H_2SO_4. B. K.

4692. **Paper chromatography of aliphatic alcohols.** Senjiro Maruta, Yoshihito Suzuki and Fumio Iwama (Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (12), 2140–2142.—When addition compounds of mercuric acetate and the crotonic esters of various alcohols (Ralston *et al.*, *Oil & Soap*, 1937, **14**, 5) are submitted to paper chromatography, good separation is effected with 90% methanol - petroleum (boiling-range 140° to 160°) (20:3) as developer for alcohols having C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18} carbon chains. The area of the spot is proportional to the amount of alcohol for <0·4 mg. Diphenylcarbazone (0·2%) in ethanol is the best colour reagent. K. SAITO

4693. **Determination of higher alcohols.** Ya. E. Shmulyakovskii. USSR Pat. 134,907 (10.1.1961).—Higher primary and secondary alcohols are converted into the corresponding alkyl nitrites, which are then determined by u.v. spectrophotometry. *Procedure*—Dissolve 10 to 20 mg of the alcohol in 10 ml of heptane, add 10 ml of water, 0·5 ml of 5N-HCl and 0·5 ml of 25% $NaNO_2$ soln. and shake for 5 min. Remove the aq. layer, add 10 ml of 0·5N-ammonium carbonate, shake for 5 min., remove the aq. layer, and measure the extinction of the heptane soln. of the alkyl nitrite in a 1-cm cell in the u.v. region, with heptane as comparison liquid. C. D. KOPKIN

4694. **Catalysts for cerium(IV) oxidimetry. Determination of polyhydric alcohols and metal chelates of 8-hydroxyquinoline.** G. G. Guilbault and W. H. McCurdy, jun. (Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 580–582.—The oxidation of glycerol, erythritol, pentaerythritol and 8-hydroxyquinoline by $Ce(SO_4)_2$ in $HClO_4$ soln. is enhanced by a Ag^I - Mn^{II} catalyst. The reaction time is between 3 and 5 min. at 90° and the end-point is indicated by the formation of the red colour of permanganate. The polyhydric alcohols can be determined with a standard deviation of 0·3 to 0·5%, while the 8-hydroxyquinolinates of Ga^{III}, In^{III}, Al^{III} and Mg^{II} can be determined with a standard deviation of 1·0%. G. P. COOK

4695. **Micro-column chromatographic method for analysis of oligosaccharides.** G. L. Miller (U.S. Army, Quartermaster Res. and Engng Center, Natick, Mass.). *Anal. Biochem.*, 1960, **1** (2), 133–140.—In the method described, the adsorbent is a mixture of activated charcoal and Celite, treated with stearic acid, and 0·2-mg samples of a mono- or oligo-saccharide, or a mixture of oligosaccharides, are used. Resolution is achieved by using gradient elution with ethanol - H_2O, and an elution rate of 1 drop per min., fractions of 10 drops being collected. The complete procedure takes 16 hr. A description of the apparatus is given. The carbohydrate content of each fraction is determined, in terms of glucose, by the addition of 3 ml of 0·2% orcinol in 70% H_2SO_4, and heating for 20 min. at 100°. The extinction of the cooled reaction product is measured at 550 mμ, with an automatic recording colorimeter. A standard curve is prepared covering the range 0·0 to 0·15 mg of glucose. Contaminants, in the form of homologues, can be determined if 2-mg samples are used. The various factors affecting the method are discussed, and reasonably quantitative recoveries are reported. D. B. PALMER

4696. **Contribution to the liquid - liquid partition chromatography of aliphatic compounds.** H. van Duin. Report No. 54. Netherlands Institute for Dairy Research, Ede. 1961, 128 pp.—Kramer and van Duin (*Anal. Abstr.*, 1954, **1**, 968) in studying the application of liquid - liquid partition chromatography to the 2,4-dinitrophenylhydrazones of aliphatic aldehydes and methyl ketones found that log R_t varied linearly with n where n is the number of C atoms in a homologous series and R_t is the corrected retention vol. (retention vol. − vol. of mobile phase in the column). The validity of this relation has been confirmed in order to apply the method to the separation and identification of aliphatic compounds as such and of complicated mixtures of aliphatic aldehydes and ketones arising from autoxidation in fatty materials. Experimental verification of the relation has also been made for derivatives of aliphatic alcohols, thiols, amines and carboxylic acids. N. E.

4697. **Determination of formaldehyde in gas mixtures by the chromotropic acid method.** A. P. Altshuller, D. L. Miller and S. F. Sleva (U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 621–625.—The modification of the chromotropic acid method for formaldehyde proposed by West and Sen (*Anal. Abstr.*, 1957, **4**, 940) was investigated. The study confirmed the findings of these workers, with only minor variations. A more detailed study of the possible interferences showed that NO_2, most aldehydes and ketones and straight-chain alcohols do not interfere significantly, while the interference of olefins and aromatic hydrocarbons can be largely eliminated under suitable sampling conditions. G. P. Cook

4698. **Polarographic determination of acraldehyde in fermentation products.** Isao Matubara and Shukuo Kinoshita (Tokyo Res. Lab., Kyowa Fermentation Ind., Yoyogi-oyama-cho, Shibuya-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 147–151.—The reduction potential of acraldehyde (**I**) shifts towards the negative region with increase in pH. At pH 8 to 10 (Kolthoff's buffer), and in the presence of 0·1M-LiCl, the height of the first wave ($E_{\frac{1}{2}} = -1{\cdot}10$ *vs.* the S.C.E.) is proportional to the concn. of **I** for <35 μg per 10 ml. Butanol and ethanol decrease the height, whilst acetone increases it. The working curve must be prepared in the presence of these solvents. **I** remains unchanged when it is bubbled with N for 15 min. This method is applied to the low-boiling distillate of fermentation broth. K. Saito

4699. **Characterisation of organic acids by means of their benzylamine salts.** G. W. H. Cheeseman and R. C. Poller (Queen Elizabeth Coll., Campden Hill Rd., London, W.8). *Analyst*, 1961, **86**, 256–259.—The organic acid (1 g) is dissolved in the minimum amount of hot ethanol or benzene and 10 ml of a 10% (v/v) soln. of benzylamine in benzene is added. The salt is pptd., usually without refrigeration or evaporation and, if necessary, may be recrystallised from ethyl acetate or a mixture of ethyl acetate with ethanol or benzene. The m.p. of the salts of 33 acids (including carboxylic and sulphonic acids and nitrophenols) are reported and also their i.r. spectra, with special reference to the absorption associated with the NH_2^+ group. A. O. Jones

4700. **Separation of malonic and succinic acids by chromatography.** M. Guillaume. *Ann. Soc. Sci. Bruxelles, Sér.* 1, 1960, **74**, 200–204.—Separation was satisfactory with an Amberlite IR-4B column (formate form) with formic acid as eluent, but the peaks were not completely separated, and the recovery was not quantitative. In ascending paper chromatography at 25°, with butyl alcohol containing 1 mole per litre of acetic acid and saturated with H_2O, the R_F values were 0·7 for succinic acid and 0·81 for malonic acid. On a cellulose column buffered at pH 3·4, the best separation was achieved with a mixture of $CHCl_3$ and butanol (22:3) containing 5% of formic acid; succinic acid was eluted last. Chem. Abstr.

4701. **Determination of mixtures of hydrazine and 1,1-dimethylhydrazine.** H. E. Malone (Edwards Airforce Base, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 575–577.—Both compounds are determined by titration of the sample in acetic acid soln. with $HClO_4$ in dioxan soln., with methyl violet as indicator. Salicylaldehyde is added to another portion of the sample and the basic hydrazone formed with 1,1-dimethylhydrazine is titrated in a similar manner; a neutral azine is formed with the hydrazine which is not titrated. The hydrazine is calculated by difference. The results are accurate to within 0·65% absolute. G. P. Cook

4702. **Thermogravimetric determination of ethylenediamine and quinine with diluric acid.** A. Berlin and R. J. Robinson (Chem. Dept., Univ. of Washington, Seattle 5, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (4), 319–328 (in English).—Thermolysis curves of the diluric acid salts of ethylenediamine and quinine were determined and both hydrated and anhydrous forms proved sufficiently stable for gravimetric use. *Determination of ethylenediamine*—The sample (1 to 11 mg) was treated with a four-fold excess of an ethanolic soln. of diluric acid. The ppt. was dried in the thermobalance between 230° and 260°, constant weight being obtained in 10 to 15 min. Methylamine does not interfere at concn. lower than that of ethylenediamine. The accuracy is $\simeq 1\%$. *Determination of quinine*—A soln. of quinine in 50% ethanol was treated with 0·02M-diluric acid in 40% methanol so that the molar ratio of diluric acid to quinine was approx. 7:1. The ppt. was washed with cold 50% ethanol saturated with diluric acid followed by cold 95% ethanol and then dried in the thermobalance between 140° and 195°. A constant weight was obtained in 15 to 20 min., corresponding to anhydrous quinine diluric acid. Cinchonine at concn. $<3{\cdot}5$ mg per ml and strychnine at concn. $<1{\cdot}0$ mg per ml do not interfere. Amounts of quinine between 2 and 40 mg were determined with a maximum deviation of 3%. A. J. Bennett

4703. **Determination of nitrogen in calcium cyanamide by decomposition with strong phosphoric acid - iodic acid.** Tomoo Takagi and Isamu Yanagida (Chem. Dept., Fac. of Sci., Kanazawa Univ., Kanazawa). *Japan Analyst*, 1960, **9** (1), 29–33.—When Ohashi's method (*Anal. Abstr.*, 1957, **4**, 3909) is applied to industrial calcium cyanamide, the effect of acetylene and of the small amount of NH_3 in the phosphoric acid (5 ml) is eliminated by preliminary heating in phosphoric acid at 260° for 3 min. K. Saito

4704. **Separation and determination of cyanamide derivatives. I. Detection of cyanamide and its**

derivatives and their hydroxymethyl compounds by paper chromatography. Masayoshi Takimoto and Kikuo Koeda (Nippon Carbide Co., Uozu, Toyama-ken). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (5), 797–799.—A mixture of sodium nitroprusside (10%), $K_3Fe(CN)_6$ (10%) and NaOH soln. (10%) (1:1:1, diluted threefold with water) is a good colour reagent for cyanamide (**I**), cyanourea (**II**), nitroguanidine (**III**), dicyandiamide (cyanoguanidine) (**IV**), thiourea, urea, guanylurea (**V**), guanidine (**VI**), aminoguanidine (**VII**), dicyanoguanidine (**VIII**) and biguanide (**IX**). Their behaviour in the solvents butanol - ethanol - water (4:1:2) and butanol - acetic acid - pyridine - water (4:1:1:2) is described. The reagent is also useful for detecting spots of hydroxymethyl derivatives of these compounds.

II. Colorimetry of guanidine, dicyandiamide and biguanide. Masayoshi Takimoto and Masaru Sawada. *Ibid.*, 1960, **63** (5), 799–803.—The above reagent was used for colorimetry. When the reaction mixture is kept in a thermostat at 25° for 30 min., the extinction at 500 mμ is proportional to the concn. of <40 μg of **VI** and **IX** per ml and <200 μg of **IV**. The error is <2% for <10 μg of **VI** and **IX** per ml and 5 to 50 μg of **IV**. The reagent must be freshly prepared and kept at 25° for 30 min. before use. Heavy-metal ions vitiate the estimation. Other cyanamide derivatives are separated by ion-exchange resin (see Part VII).

III. Determination of some cyanamide derivatives other than guanidine, dicyandiamide and biguanide. Masayoshi Takimoto and Masaru Sawada. *Ibid.*, 1960, **63** (6), 967–970.—A similar method is applicable to the determination of other derivatives. The absorption spectra are similar and Beer's law holds at 500 mμ for <10 μg of **III**, <500 μg of **V**, <5 μg of **I**, <1 mg of biuret (**X**) and <2·5 mg of urea. Thiourea (<20 mg) and **II** (<1 mg) give reproducible working curves. **VIII** reacts in a weakly acid soln. of pH 3 to 3·5. The error is <3%.

IV. Colorimetric determination of thiourea and ammonium thiocyanate. Masayoshi Takimoto and Yoko Hirano. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (9), 1414–1418.—Fearon's method [*Analyst*, 1946, **71**, 562) was modified for rapid analysis.

V. Colorimetry of urea. Masayoshi Takimoto and Yoko Hirano. *Ibid.*, 1960, **81** (9), 1418–1421.—The coloration of urea with dimethylglyoxime and thiosemicarbazide (Okuma, *Anal. Abstr.*, 1957, **4**, 168) was applied to the photometric determination of 0·2 to 2 μg of urea per ml at 525 mμ.

VI. Mutual separation of cyanamide derivatives by ion-exchange resin. Masayoshi Takimoto and Toru Yatsuo. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (11), 1938–1941.—**VI**, **IX** and **V** are adsorbed on cation exchanger Amberlite IR-120 (H^+ form) and **VI** and **IX** are separated by elution with N-HCl (≃100 ml for 0·001 mole) and 3N-HCl, respectively. Separation of **V** and **VI** is effected with 0·1M-LiCl. **I**, **II** and SCN^- are adsorbed on anion exchanger Amberlite IRA-410 and separated from the other compounds.

VII. Micro-determination of cyanamide derivatives. Masayoshi Takimoto and Toru Yatsuo. *Ibid.*, 1960, **63** (11), 1941–1944.—By the use of the results mentioned above the determination of **I**, **IV**, urea, thiourea and **VI** was studied. **I** and thiourea are pptd. with ammoniacal Ag^+ soln., and **VI**, Ag^+ and NH_4^+ are removed by Amberlite IR-120; **IV** can then be determined photometrically. By passing the sample mixture (2 to 3 ml) through a column (diameter 0·8 mm, length 20 cm) of Dowex 1-X10 (48 to 80 mesh), **I** is adsorbed, and **VI**, thiourea and **IV** can be determined photometrically in the 0 to 20-ml, 20 to 60-ml, and 60 to 140-ml fractions of the aq. eluate, respectively. **I**, thiourea and urea are similarly determined in the eluate from Dowex 50-X12 in the 0 to 15-ml, 20 to 140-ml, and 140 to 260-ml fractions, respectively. For the separation of **IV**, **VI** and **X**, the two last are adsorbed on Amberlite IR-120, **IV** is determined in the first 60-ml fraction of the aq. eluate and **VI** and **X** are separated as described in Part VI. K. SAITO

4705. **Fluorimetric titration of sulphides and mercaptans [thiols] with tetramercuric acetate-fluorescein [tetra(acetoxymercuri)fluorescein].** M. Wroński (Inst. Chem. Technol., Univ. Łódź, Poland). *Z. anal. Chem.*, 1961, **180** (3), 185–188 (in German).—The method is based on the quenching of the fluorescence of the reagent (**I**) by sulphides and thiols. *Procedure*—Dilute the test soln. suitably with 0·8% formaldehyde soln. Transfer an aliquot (25 ml) to a tall-form beaker (diameter 36 mm) and add N-NaOH (0·5 ml). Titrate with **I** soln. ($4·2 \times 10^{-3}$N in 0·01N-NaOH) with stirring, measuring the fluorescence after each addition. Determine the end-point graphically. As little as 0·8 μg of H_2S per litre may be determined. The results were high by 5%; a suitable correction reduced this to ≃2%. Methanethiol gave a mean error of ±7% (0·35 to 12·4-μg samples). Cysteine gave poor results. G. RUSSELL

4706. **Effect of formation of insoluble polysilver salts on argentimetric titration of mercapto-acids.** E. M. Carr and M. Bit-Alkhas (Toni Co., Chicago, Ill., U.S.A.). *Anal. Biochem.*, 1960, **1** (2), 158–167.—Evidence is presented that the high results observed when substances possessing both thiol and carboxylic acid functions are titrated in ammoniacal media with $AgNO_3$ are due to the formation of salts having the general formula AgS·RCOOAg. Four mercapto-acids (mercaptoacetic, β-mercaptopropionic, mercaptosuccinic and αα′-dimercaptoadipic) were determined by three volumetric methods, *viz*, iodimetric, alkalimetric and argentimetric. A soln. of each acid was also treated with a moderate excess of ammoniacal $AgNO_3$, and the ppt. produced was analysed for Ag, S and -SH, and also by infra-red spectroscopy. It is postulated that the ease with which Ag combines with the carboxylate ion of acids of this type is favoured by the crystal structure of the resulting compound. D. B. PALMER

4707. **Colour reactions of organosilicon compounds and their use for photometric analysis.** A. P. Kreshkov and V. A. Bork. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (3), 410–415; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D203.—Colour reactions are described for phenoxysilanes, trichlorosilane, $SiCl_4$ and aminosiloxanes. Photometric procedures are given for the analysis of some organosilicon compounds, including the determination of phenoxy-groups, of alcohol, phenol and $SiCl_4$ impurities in alkoxysilanes and of trimethylchlorosilane. A. BURWOOD-SMITH

4708. **Direct determination of organometal derivatives by gas chromatography.** M. A. Molinari, J. Lombardo, O. A. Lires and G. J. Videla (Com. Nac. Energía Atómica, Buenos Aires). *An. Asoc. Quim. Argentina*, 1960, **48** (4), 223–227.—Solutions

of organomagnesium derivatives are analysed by hydrolysis with conc. H_3PO_4 in a micro-reactor and passing the hydrocarbons evolved through a by-pass injector into a gas-chromatographic apparatus (with an activated silica-gel column, for C_1 to C_3 hydrocarbons), calculating the amounts from the peak areas in the usual way. L. A. O'NEILL

4709. **Colorimetric determination of phenols in water with 4-aminophenazone.** B. P. Ershov and F. B. Borisov. *Plast. Massy*, 1960, (6), 66–68; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D196.—The photometric determination of phenols in sewage by the use of 4-aminophenazone (**I**) in the presence of $K_3Fe(CN)_6$ is improved; the reaction is carried out without a buffer soln. To the sample add 250 ml of water, acidify with H_2SO_4, add 25 ml of 10% $CuSO_4.5H_2O$ soln. and distil off the volatile phenols. To 10 ml of distillate (1 to 10 mg of phenols per litre) add 0·5 ml of aq. NH_3 (1:1), 0·2 ml of $K_3Fe(CN)_6$ soln. and 0·2 ml of a 2% **I** soln., make up to 20 ml, and after 2 min. measure the extinction at 541 mμ. *Ortho-* and *meta*-substituted phenols give analogous colours; *para*-substituted phenols (<15%) do not interfere.
C. D. KOPKIN

4710. **Improved technique for recording chromatograms. Analysis of cresol mixtures.** F. Alderweireldt (Lab. Organ. Chem., Univ. Ghent, Belgium). *J. Chromatography*, 1961, **5** (2), 98–102 (in English).—A device for introducing samples without interrupting the flow of solvent, and an improved flow-cell for measuring the absorption of the solution in the u.v., are described. The apparatus has been used in the separation of *o-*, *m-* and *p*-cresol, with silica gel impregnated with a phosphate buffer as stationary phase and 2,2,4-trimethylpentane as the mobile phase. The relative concn. of the cresols were measured by recording the % transmission of the eluent at 276 mμ as it emerged from the column. R. M. ROWLEY

4711. **Paper chromatography of mono- and di-hydroxybenzoic acids.** H. Krieger (Med. Res. Lab., Lääke Oy, Turku). *Suomen Kem., B*, 1961, **34**, (4), 50–52 (in German).—Published data on the R_F values of mono- and dihydroxy-benzoic acids in various solvent systems are tabulated. Two solvent systems were chosen as being most suitable for the chromatography of hydroxybenzoic acids, *viz*, an alkaline solvent, isopropyl alcohol - 7N-aq. NH_3 (4:1), and an acid solvent, benzene - acetic acid - water (8:11:4). The R_F values for mono- and di-hydroxybenzoic acids and salicyluric acid in these two solvents were plotted against each other to correlate R_F value and chemical structure. The results are discussed. S. M. MARSH

4712. **Study of the reduction waves of the isomers of nitrophenol by means of the alternating-current polarograph.** Takeo Takahashi and Hideko Shirai (Inst. of Ind. Sci., Univ. Tokyo, Japan). *Talanta*, 1961, **8** (4), 177–186 (in English).—The d.c. polarography of the isomers of nitrophenol suffers from the disadvantage that in certain basal soln. the reduction waves are not solely diffusion-controlled. The a.c. polarograms are found to have wave-heights proportional to the concn. of the isomers in KOH and NH_4Cl - aq. NH_3 basal soln.; these wave-heights are not affected by change in concn. of the supporting electrolyte, but are reduced in size when produced in acidic media.
G. S. ROBERTS

4713. **Paper chromatography and paper electrophoresis of dinitrophenols.** Wataru Funasaka and Tsuguo Kojima (Dept. Ind. Chem., Fac. of Engng, Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1960, **9** (1), 33–37.—By the use of a filter-paper impregnated with citrate or acetate buffer, *p*-nitrophenol (**I**), 2,4-dinitrophenol (**II**), 2,6-dinitrophenol and 2,4,6-trinitrophenol (**IV**) are separated with amyl alcohol - benzene - 0·5M-acetate buffer (pH 4) (4:1:5). The R_F values are 0·92, 0·50, 0·35 and 0·12 for **I**, **II**, **III** and **IV**, respectively. By the use of acetate buffer of pH 3·2 to 3·6, paper electrophoresis can be effected within 1·5 hr. at 500 V.
K. SAITO

4714. **Determination of chlorotrinitrobenzene in admixture with chlorodinitrobenzene.** A. A. Oksuzyan, A. G. Gorst and N. F. Vasil'eva. USSR Pat. 135,683 (15.2.1961).—A boiling soln. of the chlorotrinitrobenzene (**I**) in 10 to 15 times its weight of ethanol is titrated with Na_2SO_3 soln. in the presence of MgO or $MgCO_3$; **I** reacts with Na_2SO_3 to give di(trinitrophenyl) sulphide, while chlorodinitrobenzene does not react. At the end-point the soln. becomes dark red because of resinification.
C. D. KOPKIN

4715. **Adsorption of amines on cation-exchange resins.** S. R. Watkins and H. F. Walton (Univ. of Colorado, Boulder, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (4), 334–342 (in English).—Aniline, benzylamine, pyridine, piperidine and n-butylamine are adsorbed by sulphonated polystyrene resins in excess of the ion-exchange capacity of the resin when water is the solvent, but not when the solvent is methanol, acetic acid or dioxan. It is possible to separate pyridine from the other amines by eluting with ethanolic HCl, and benzylamine can be separated by elution with aq. HCl. Fine-mesh resins should be used as the diffusion of large molecules within the resin is slow.
A. J. BENNETT

4716. **Determination of *N*-*o*-bromobenzyl-*N*-ethyl-*NN*-dimethylammonium toluene-*p*-sulphonate.** I. Gyenes (Pharm. Factory Kőbánya, Budapest). *Magyar Kém. Foly.*, 1961, **67** (4), 162–165.—Three methods for the determination of this compound (**I**) by means of Na tetraphenylborate (**II**) are described. (*i*) Gravimetric method, by pptn. of bromobenzyl-ethyldimethylammonium tetraphenylborate (**III**) (*cf.* Gautier, *Angew. Chem.*, 1955, **67**, 755). (*ii*) Volumetric method in non-aq. medium in which the gravimetric procedure for pptn. of **III** is followed by dissolution of the dry ppt. in ethyl methyl ketone - acetic anhydride (1:1) and titration of the soln. with 0·01N-$HClO_4$ to methyl violet. (*iii*) Volumetric method in aq. medium. A dried sample of **I** is dissolved in water and $CHCl_3$ is added. The titration is carried out in a separating-funnel, 0·02M-**II** being added until the indicator (Tropaeolin OO or dimethyl yellow) ceases to colour the $CHCl_3$ layer. The relative errors of the three methods are quoted as (*i*) ±0·6%, (*ii*) ±0·2% and (*iii*) ±0·7%. B. VASZKO

4717. **Spot-test detection and colorimetric determination of aniline, naphthylamine and anthramine derivatives with azobenzene-4-diazonium fluoroborate.** E. Sawicki, J. L. Noe and F. T. Fox (Div. of Air Pollution, Taft San. Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Talanta*, 1961, **8** (4), 257–264 (in English).—Aniline,

1- and 2-naphthylamines, 1- and 2-anthramines and their *N*-alkyl and *NN*-dialkyl derivatives can be detected or determined by coupling with azobenzene-4-diazonium fluoroborate. The reaction can be applied to spot-test, micro-tube or colorimetric procedures, and merely involves mixing a soln. of the amine in 2-methoxyethanol with a 0·1% soln. of the reagent, heating and making acid with conc. HCl. The intense colours produced are measured in the range 610 to 675 mμ. Some interference was observed, particularly from diphenylamine and its derivatives, indole and carbazole. G. S. ROBERTS

4718. **Ultra-violet, visible and fluorescence spectral analysis of polynuclear hydrocarbons.** E. Sawicki, T. R. Hauser and T. W. Stanley (Public Health Serv., Cincinnati, Ohio, U.S.A.). *Int. J. Air Pollut.*, 1960, **2**, 253–272.—By the use of a new simple, sensitive, and specific test, benzo[*a*]pyrene can be identified unequivocally in a mixture of 50 polynuclear hydrocarbons containing benzene, naphthalene, anthracene, phenanthrene, benzo[*a*]anthracene, benzo[*c*]phenanthrene, chrysene, pyrene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, perylene, benzo[*ghi*]perylene, anthanthrene and coronene. The ultra-violet, visible, activation and fluorescence spectra in pentane of a large number of polynuclear hydrocarbons are presented, and the fluorescence intensities of the different hydrocarbons are compared. The sensitivity of the fluorimetric methods is of the order of parts per 10^9. The quenching effect of a fairly high concn. of miscible compounds in a mixture as it affects fluorimetric analysis for some particular hydrocarbons is also discussed. CHEM. ABSTR.

4719. **Determination of acridine by potentiometric titration in acetic acid.** P. Ramachandra Naidu and V. R. Krishnan (Sri Venkateswara Univ., Tirupati, India). *Anal. Chem.*, 1961, **33** (4), 497–498.—Acridine in acetic acid soln. can be titrated potentiometrically with $HClO_4$ to an accuracy within 0·5 mg in the range 28 to 180 mg. G. P. COOK

4720. **Analysis of terpenes and perfumes by gas chromatography. I. Analysis of terpene hydrocarbons.** Tamon Matsuura, Hisashi Komae, Takaaki Aratani and Shuichi Hayashi (Fac. of Sci., Hiroshima Univ., Senda-machi, Hiroshima). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (10), 1761–1765.—Among seven kinds of fixed phase, tritolyl phosphate (**I**) on kieselguhr and squalane on kieselguhr bring about good separation for 2-bornene, α-pinene, tricycene, camphene, (+)-limonene, *p*-cymene, 1,8-cineole, terpinolene and α-terpinene with He as carrier gas. **I** gives better separation, the retention time increasing in the order given. β-Pinene is decomposed. 1,8-Cineole and cyclohexanol are good internal standards. K. SAITO

4721. **Improvement of the oxime method for camphor.** Yoshiharu Matsubara, Shoji Wakabayashi and Minoru Morita (Saisei Camphor Co., Wakihamacho, Fukiai-ku, Kobe). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (7), 1250–1251.—The method of Fritz *et al.* for carbonyl determination (*Anal. Abstr.*, 1959, **6**, 3553) was applied with modifications. By the use of ethanol as solvent, the oxime formation is complete within 3 hr. at 85°. *Procedure*—Heat the sample (0·35 to 0·4 g) under reflux with 2-dimethylaminoethanol (0·7M in ethanol, 10 ml) and hydroxyammonium chloride (M in 90% ethanol, 15 ml) at 85° for 3 hr. Cool, add Martius yellow (C.I. Acid Yellow 24) soln. (0·0667 g in 50 ml of ethanol containing 0·004 g of methyl violet) and titrate with 0·2M-$HClO_4$ in 2-methoxyethanol. K. SAITO

4722. **Determination of piperazine derivatives. Determination of piperazine, *N*-hydroxyethylpiperazine and *NN*-di(hydroxyethyl)piperazine present together in non-aqueous solution.** E. Toldy, F. Csillag, T. Bobák and I. Gyenes (Res. Inst. for the Pharmaceutical Ind., Budapest). *Magyar Kém. Foly.*, 1961, **67** (4), 180–182.—The amounts of these compounds present in a mixture are determined by a volumetric procedure involving three titrations with $HClO_4$. Piperazine (**I**) and *N*-hydroxyethylpiperazine (**II**) are first separated from *NN*-di(hydroxyethyl)piperazine (**III**) by pptn. with CS_2 from a soln. of the mixture in $CHCl_3$. The pptd. **I** and **II** are then dissolved in dry methyl cyanide and titrated with 0·05N-$HClO_4$ to crystal violet indicator. A separate estimate of **II** is obtained by similar titration after acetylation of the methyl cyanide soln. of **I** and **II** with acetic acid - acetic anhydride (1 : 4). **III** is determined by $HClO_4$ titration of the $CHCl_3$ soln. after pptn. and separation of **I** and **II**. If **III** is absent, the pptn. step may be omitted. Tests on synthetic mixtures and industrial samples are reported. B. VASZKO

4723. **An electron paramagnetic resonance investigation of vanadium in petroleum oils.** A. J. Saraceno, D. T. Fanale and N. D. Coggeshall (Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 500–505.—A rapid and accurate method is described for the determination of quadrivalent vanadium in petroleum oils. Vanadyl aetioporphyrin is used as a standard and quant. determination in the range of 0·1 to 200 p.p.m. is feasible. Good agreement is found between electron paramagnetic resonance determinations and chemical determinations on a wide range of distillates, residues and full crudes. C. B. BAINES

4724. **Determination of traces of nickel and vanadium in petroleum distillates. An X-ray emission spectrographic method based on a new rapid ashing procedure.** J. E. Shott, jun., T. J. Garland and R. O. Clark (Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 506–510.—The sample (10 g) is mixed with 1 ml of cobalt soln. (Co naphthenate or a similar compound in xylene; 1 ml ≡ 0·1 mg of Co) as internal standard and 3 g of benzenesulphonic acid is added. The inclusion in the internal standard soln. of 1 mg of Mg per ml, *e.g.*, as the salt of 2-ethylhexoic acid, assists in the subsequent collection of the ash. The mixture, in a platinum dish, is heated to b.p. and ignited. The ash is further ignited at 600° to 700° until a C-free residue is obtained. The cooled ash is mixed with 5 ml of iso-octane and transferred to a glass-fibre filter, and suction is applied to give an even distribution on the disc, which is then removed and examined in an X-ray emission spectrograph. Nickel is determined in the range 0·01 to 0·4 p.p.m. and V in the range 0·01 to 2·5 p.p.m. Recoveries by this rapid ashing technique are in fair agreement with those obtained by wet-ashing with H_2SO_4. T. R. ANDREW

4725. Vapour-phase separation of mixtures of hydrocarbons and organic sulphur compounds by chromathermography. B. V. Alvazov. Publ.: "Khromatografiya, ee Teoriya i Primenenie", Akad. Nauk SSSR, Moscow, 1960, 438–440; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D193.—The application of chromatographic apparatus for the preparative separation of petroleum fractions boiling at 200° to 300° is described. The apparatus comprised four glass columns of length 2·75 metres and diam. 8 mm joined in parallel; the diam. of the lower part of the condenser column was 2 mm; the height of the adsorbent layer, in the central part of the column, was 75 cm. The sorbents used were types ASK and KSM silica gel and their mixture; the carrier gas was N or CO_2, used at a rate of 300 ml per min. The rate of movement of the furnaces was 0·2 cm per min. From the experiments carried out, it is concluded that mixtures of various groups of hydrocarbons and organic sulphur compounds can be separated. Separation can be made of mixtures of naphthenic and other aromatic hydrocarbons with alkyl sulphides and cyclic sulphides, mixtures of bicyclic aromatic compounds with bi- and tri-cyclic sulphides, and mixtures of aliphatic sulphides and mono- and bi-cyclic sulphides. C. D. Kopkin

4726. Gas - liquid chromatographic analysis of aromatic hydrocarbons boiling between 202° and 280° in a low-temperature coal tar. Ta-Chuang Lo Chang and C. Karr, jun. (Low-Temp. Tar Lab., Bureau of Mines, U.S. Dept. of the Interior, Morgantown, W. Va.). *Anal. Chim. Acta*, 1961, **24** (4), 343–356 (in English).—Two columns were used packed with 25% Apiezon L grease on 30 to 60-mesh firebrick. One column was used at 200° for fractions boiling between 202° and 233°, and the other at 220° for fractions boiling between 233° and 275°. The carrier gas was He (100 ml per min.). Forty-eight compounds were identified by determination of their retentions relative to 1,3,5-triethylbenzene at 200° and 220° and by examination of u.v. and i.r. spectra. Quant. determinations were made on most of the compounds, 20 of which were alkylnaphthalenes. When the log. of the relative retentions at 220° for alkylnaphthalenes having an equal no. of C atoms in the alkyl groups were plotted against their b.p. a straight line resulted. Alkylbenzenes showed a similar relation. The values for C_{11}, C_{12} and C_{13} compounds lay on 3 parallel lines. A difference in the slope of these lines was observed among the 3 groups—benzenes, naphthalenes and biphenyls, that of the benzenes being 0·0113, that of the naphthalenes 0·0098, and that of the biphenyls 0·0164. A. J. Bennett

4727. Recent methods for analysing waters from coal distillation. U. Behrens, U. Ringpfeil and A. Gabert. *Chem. Tech., Berlin*, 1960, **12** (11), 672–675.—Full descriptions are given of paper and gas - liquid chromatographic methods for the separation and quant. and qual. determination of the individual mono- and poly-hydric phenols and fatty acids in the various waste waters from brown-coal distillation or coking. Several methods are described for evaluating the amounts of the separated phenols and acids in each case, including an automatic titration method in which the separated acids are titrated in an automatically operating and recording apparatus; the separated phenols are oxidised to CO_2 and the CO_2 is titrated similarly. Paper chromatography is suitable for general works practice and can be applied to the water itself (after suitable adjustment of concn.); for highly accurate work, separation by gas - liquid chromatography is necessary. H. L. Whitehead

4728. Detection, isolation and identification of surface-active agents. M. J. Rosen (Chem. Dept., Brooklyn Coll., Brooklyn, N.Y., U.S.A.). *J. Soc. Cosmet. Chem.*, 1961, **12** (2), 98–106.—An outline of methods is given, with 12 references, covering synthetic organic materials, including soaps, but not inorganic materials and natural products possessing surface-active properties. Topics discussed include the detection of ionic surfactants by dye-solubilising tests, colour-change tests and dye-transfer tests (tests for non-ionic surfactants are not discussed, except for the "heat test" for non-ionic ethylene oxide compounds, because of their limited applicability and sensitiveness to interference), the isolation of the surfactant by solvent extraction or ion-exchange procedures, and the identification of the group to which the isolated compound belongs by tests for "additional" elements (N, S, P or metal) and for functional groups, and final identification of the individual compound by physical properties, mol. or equiv. wt. or quant. elementary analysis. R. E. E.

4729. Volumetric determination of surface-active quaternary ammonium salts using Marmé's reagent. Toyozo Uno and Koichiro Miyajima (Fac. Pharm., Univ. Kyoto). *Chem. Pharm. Bull., Japan*, 1961, **9** (4), 326–327 (in English).—When a drop of methyl orange soln. is added to a soln. of a quaternary ammonium salt having a long-chain alkyl group, it forms a 1:1 complex that does not show a red colour at pH 3. When the mixture is titrated with K_2CdI_4 (*cf.* Buděšínský and Vaníčková, *Anal. Abstr.*, 1957, **4**, 1579) first the excess of surfactant is pptd., then that in the complex, and the liberated methyl orange gives a red end-point. *Procedure*—To the test soln. (0·02M to 0·002M) (10 to 20 ml) add a drop of 0·005M-methyl orange, adjust the pH to 3 with HCl and titrate with 0·01N-K_2CdI_4 to a red end-point. Results for 7 quaternary ammonium salts are given, and agree well with those by the Na tetraphenylborate method (Uno *et al.*, *J. Pharm. Soc. Japan*, 1960, **80**, 153). The method can be used between pH 2·6 and 3·2 for concn. of quaternary ammonium salt >0·002M. The addition of more than 2 drops of 0·005M-methyl orange renders the end-point less sharp and leads to a positive error. Quaternary ammonium salts having 8 C atoms in the chain (*e.g.*, benzyldimethyloctylammonium bromide and trimethyloctylammonium bromide), which can be determined by the tetraphenylborate method, cannot be determined by the present procedure. R. E. E.

4730. Examination of lemon oil by gas - liquid chromatography. III. The oxygenated fraction. J. R. Clark and R. A. Bernhard (Dept. of Food Sci. and Technol., Univ. California, Davis, U.S.A.). *Food Res.*, 1960, **25** (6), 731–738.—Samples of the oxygenated fraction of cold-pressed Californian lemon oil, isolated by a modification of the procedure of Kirchner and Miller (*Ind. Eng. Chem.*, 1952, **44**, 318) have been examined with LAC-2-R446 (adipate polyester of diethylene glycol partly cross-linked with pentaerythritol), LAC-4-R777 (succinate polyester of diethylene glycol) and DEGS (diethylene glycol succinate) as stationary phases (20%) on Sil-O-Cel C-22 diatomaceous earth. For the LAC phases, stainless-steel tubes (10 ft. × 0·25 in.) were

used with a He flow-rate of 90 ml per min. at 150°, and a 6-ft. tube at 112° and a flow-rate of 140 ml per min. for the DEGS phase. On the LAC chromatograms 37 peaks were observed, 23 of which were identified; on the DEGS chromatograms 29 major and 6 minor peaks were observed, of which 15 were identified. Relative corrected retention vol. are tabulated. (*Cf.* Bernhard, *Anal. Abstr.*, 1961, **8**, 201, 1304.) R. E. E.

4731. **Determination of citronellol in admixture with geraniol. Further studies of formylation reactions by gas - liquid chromatography.** D. Holness (Proprietary Perfumes Ltd., 117–121 Grange Rd., London, S.E.1). *Analyst*, 1961, **86**, 231–239.—A previous report from the Essential Oils Sub-Committee of the Analytical Methods Committee of the Society for Analytical Chemistry on methods of hot formylation of mixtures of citronellol and geraniol (*Ibid.*, 1959, **84**, 690) confirmed to a certain extent the work of Pfau (*J. prakt. Chem.*, 1921, **102**, 276), who showed that citronellol is not converted into its formate but that its chief products are the mono- and di-formates of 3,7-dimethyl-octane-1,7-diol, and that polymers of uncertain composition could also originate from the alcohols. In the present work the nature of the compounds giving rise to peaks in the gas - liquid chromatograms of the formylated products was investigated and also the effects of variations in the reaction conditions on the deviations from the correct analytical results. It was found that the theory of hot formylation takes no account of several important side reactions, and it is finally concluded that formylation cannot serve as the basis of an accurate analytical method, however much the working conditions are modified. A. O. Jones

4732. **Determination of nitrogen in cellulose nitrate and nitric acid. II. Rapid determination by titration with ferrous sulphate.** Tetsuro Murakami (Kogakuin, Tsunohazu, Shinjuku-ku, Tokyo). *Japan Analyst*, 1960, **9** (2), 100–105.—Bowman's method (*Ind. Eng. Chem.*, 1915, **7**, 766) was modified. A rapid dissolution of cellulose nitrate in H_2SO_4 (80 to 95%) below 10° is effected by first dissolving the sample in acetone, adding water to re-precipitate the sample as a fine powder. *Procedure*—Dissolve the sample (0·5 g) in acetone (20 ml), add water (20 ml) with vigorous stirring, and evaporate to <4 ml with suction in the presence of small glass beads. Add H_2SO_4 (95%) (100 ml) with vigorous shaking to the ice-cooled residue, the first 10-ml portion being added during 1 min. Titrate the clear soln. with $FeSO_4$ soln. (176 g of $FeSO_4.7H_2O$ in 400 ml of water mixed with 500 ml of 60% H_2SO_4 and made up to 1 litre). The rate of titration must be <2 ml per min. The time taken for a determination is <40 min. K. Saito

4733. **Neutron absorption estimation of boron preservatives in timber.** R. J. Griffiths and R. Cockcroft (Nat. Inst. for Res. in Nucl. Sci., Harwell, England). *J. Inst. Wood Sci.*, 1961, (7), 73–77.—Two rapid and non-destructive methods for determining up to $\simeq 2\%$ (as H_3BO_3) of preservative by measuring the neutron-flux attenuation caused by the sample are described. In the first, neutron flux from a reactor is used to irradiate sawdust and a result, accurate to within $\pm 0{\cdot}3\%$, can be obtained in $\simeq 1$ hr.; a correction is applied for moisture content. In the second, a plutonium - beryllium neutron-source is used and the sample (a small block) is surrounded by untreated wood to minimise neutron scatter; the error is $\pm 4\%$ after counting for 1 hr. with a BF_3 detector. When improved, the second method could be used for routine analyses of many small samples, *e.g.*, of building boards containing up to 15% of B. W. J. Baker

4734. **Determination of "Hibbert compounds."** O. Töppel. *Holzforschung*, 1960, **14** (5), 139–146 (in German).—"Hibbert compounds" or "Hibbert bodies" are the products obtained on ethanolysis of ligniferous materials, such as wood, pulp or spent sulphite liquor. They include vanillin, syringaldehyde, *p*-hydroxybenzaldehyde, α-oxo-β-hydroxy-(or ethoxy-)guaiacyl- (or syringyl- or *p*-hydroxyphenyl-)propane, and α,β-dioxoguaiacyl- (or syringyl- or *p*-hydroxyphenyl-)propane. A comprehensive study of the colour reactions of these compounds was made, using 15 different spray reagents, some of which are also applicable to chromatography. Using spruce lignin as an example, the possible application of these reactions to routine analysis was investigated, including sample preparation, method of ethanolysis, choice of solvent and spray reagents, light absorption of Hibbert compounds on paper and in chromatographic eluates, and determination of optical extinction coefficients. Relative amounts of Hibbert compounds could be determined by measuring paper chromatograms directly in monochromatic u.v. light or after colour development with Bright's soln. Absolute determinations were possible by elution of chromatograms and application of Bright's soln. Abstr. Bull. Inst. Pap. Chem.

4735. **TAPPI standards; routine control methods.** Tech. Ass. Pulp and Pap. Ind. *TAPPI*, 1961, **44** (1), 112A-116A.—The following TAPPI standards and routine control methods are presented—Rosin in paper and paperboard; Proposed revision of TAPPI Official Std. T 408 m-52—8 ref., p. 112A-114A; RC292. Determination of specific gravity of liquid resins (hydrometer method), p. 115A; RC293. Measurement of pH of liquid resin syrups, p. 115A; and RC294. Measurement of pH of liquid resin syrups at pH 11 or higher, p. 115A-116A. Abstr. Bull. Inst. Pap. Chem.

4736. **Determination of cottonised bast fibre in blends with rayon staple.** E. Frieser (Fed. Treasury Admin., Vienna). *Textil-Praxis*, 1960, **15**, 284–290.—Nine chemical methods, in which the rayon was preferentially dissolved, and 2 physical methods, in which the differentially dyed fibres were either sorted or counted, were applied to the analysis of blends of cottonised bast fibre and rayon staple. Of the chemical methods, 2 failed to dissolve the rayon and 5 others gave high weight losses of the other component. By the most accurate method, 5 g of fibre was heated for 30 min. at 40° in 150 ml of 40% aq. formaldehyde, then washed, and dried for 3 hr. at 105° to 110°; 3 g of this pretreated fibre in 150 ml of soln. consisting of 85 parts of 85% formic acid and 15 parts of $CaCl_2$ was heated with 5 g of paraformaldehyde for 25 min. at 90° and the residue was filtered off, washed with H_2O, dried for 3 hr. at 105° to 110°, and weighed. Corrections were made for weight loss (7·3%) of the cottonised bast fibre and for the different moisture regain of the components. Chem. Abstr.

4737. **Quantitative determination of silk in fibre blends.** E. Frieser. *Textilrdsch.*, 1960, **15**, 238–248.—Older and newer solvent methods are re-examined for the separation of Schappe silk from

cotton, linen, wool, viscose, cuprammonium rayon, acetate, Ardil, polyamide, poly(vinyl cyanide), polyester, and poly(vinyl chloride) fibres. The following reagents are used—5% KOH; N-NaOCl; ammoniacal nickel hydroxide soln.; Cu^{3+} - glycerol - NaOH; anhydrous $ZnCl_2$ (10 g) in 85% formic acid (100 ml); 85% formic acid; acetone; dichloromethane; and cupric ethylenediamine soln. New correction factors are given, which give better accuracy. Tussah silk is generally less soluble than Schappe silk. CHEM. ABSTR.

4738. **Determination of natural and synthetic polyamides in fibre blends.** E. Frieser. *Textilrdsch.*, 1960, **15**, 65–74.—Fibres made from regenerated proteins (**I**) and polyamides were compared with wool, silk, and cellulose fibres by qual. and quant. methods. The casein fibres examined were Fibrolane BX, Merinova, Aralac, Lanital S; those from soya protein, Silkool and Prolon; those from peanuts, Ardil and Sarelon; and those from zein, Vicara and Cuprama SK. The qual. tests consisted of the ninhydrin reaction, the Morse test, swelling in conc. H_2SO_4, solubility in N-HCl, dyeing with Alizarin red AS (C.I. Mordant Red 3), and a P_2O_5 test. For the quant. determination of **I**, methods based on NaOH, $Ba(OH)_2$, H_2SO_4 and peracetic acid were approximately equally accurate. For mixtures of **I** with cotton, the NaOCl method was preferred to the trypsin and pepsin methods. For mixtures with regenerated cellulose the methods based on NaOCl, KOH, KOH - NaOCl, and the modified formic acid - $ZnCl_2$ methods are applicable. A table of the amino-acid contents of Ardil, Lanital, Vicara, and Silkool is included.
CHEM. ABSTR.

4739. **Characterisation of different types of polyamide fibres by infra-red spectrography.** P. Bouriot. *Bull. Inst. Text. France*, 1961, (92), 93–99 (in German).—The i.r. spectra of fibres from polyamides **6**, **6–6**, **7** and **11** differ distinctly from each other in the region between 1500 and 850 cm^{-1}, and certain characteristic features of these spectra can be attributed to the CO·NH groups and to the equal numbers of CH_2 groups. Between 3500 and 1500 cm^{-1}, the spectra are very similar, indicating that their association energy due to hydrogen-bonding is comparable. The spectrum of polyurea fibre in this region differs from that of the polyamides examined; this is probably due to a different arrangement of the structural elements responsible for the hydrogen-bonding.
SHIRLEY INST. ABSTR.

4740. **Textiles: quantitative determination of the resin content in finished textiles.** Swiss Standards Association. *Textilrdsch.*, 1961, **16** (3), 126–127.—The Swiss specification SNV 95 6 49 describes the preparation of the sample, apparatus and reagents, and the method for the quant. determination of urea - formaldehyde, thiourea - formaldehyde, cyclic ethyleneurea - formaldehyde, and melamine - formaldehyde condensation products, applied to textiles for improving their shrinking, creasing and swelling properties. In the test-report, the acid-soluble portion is given as the percentage weight loss of the initial, absolutely dry sample, after it has been washed according to the specification. SHIRLEY INST. ABSTR.

4741. **Detection of resins on white fabrics.** W. Ernst and M. Sorkin. *Textilrdsch.*, 1960, **15**, 433–434.—Colour reactions are described and tabulated for the following resins—poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride), epoxy resin, urea - formaldehyde, thiourea - formaldehyde, methylated urea - formaldehyde, melamine - formaldehyde, methylated melamine - formaldehyde and dicyandiamide. The reagents used are Neocarmine W, Neocarmine B, Du Pont Stain 4, $AgNO_3$ and gold chloride. CHEM. ABSTR.

4742. **Development of a test method for the determination of free formaldehyde in photographic papers, melamine resin solutions and melamine resins.** G. Schulz. *Zellstoff u. Papier*, 1960, **9** (11), 421–425 (in German).—Conventional methods of formaldehyde determination are reviewed. Most are based on the extraction of formaldehyde with water, which also dissolves free hydroxymethyl groups, fillers, cellulose fibres, and other components. The method and apparatus developed and described avoid subsequent separations by effecting the sole and complete removal of formaldehyde in the vapour phase by heating the sample in a stream of air at 150° to 160°. A paper sample of 300 to 400 sq. cm requires 90 min. of heating. The formaldehyde is determined in aq. soln. by treatment with Na_2SO_3 and titration of liberated NaOH. Agreement with the iodine method is satisfactory.
ABSTR. BULL. INST. PAP. CHEM.

4743. **Detection of "additional elements" in plastic materials by the oxygen-flask combustion method.** J. Haslam, J. B. Hamilton and D. C. M. Squirrell (I.C.I. Ltd., Plastics Div., Bessemer Rd., Welwyn Garden City, Herts., England). *Analyst*, 1961, **86**, 239–248.—The sample (polymer, polymeric composition or plasticiser) is burnt in an oxygen flask (*Ibid.*, 1960, **85**, 556; *Anal. Abstr.*, 1960, **7**, 4383) with electric firing, and the products of combustion are absorbed in NaOH soln. The absorbent is then diluted to a known vol. and tests for the additional elements (*i.e.*, elements other than C, H and O) are applied to aliquot portions. Nitrogen is detected as NO_3^- by the colorimetric method of Peach (*Analyst*, 1958, **83**, 644), in which the sample soln. is added to a soln. of resorcinol in glacial acetic acid and addition of $(NH_4)_2SO_4.FeSO_4$ then produces a green colour in the presence of NO_3^-. Sulphur is detected with $BaCl_2$ after acidification and addition of a protective colloid. Phosphorus is detected by formation of molybdenum blue, with ascorbic acid as reducing agent. Fluorine is detected by the alizarin complexan - cerous nitrate test (Belcher *et al.*, *Anal. Abstr.*, 1959, **6**, 4759; 1960, **7**, 3287). Chlorine is detected by the mercury thiocyanate test of Sergeant *et al.* (*Analyst*, 1959, **84**, 251), but in the (unusual) presence of Br (detected by a fluorescein reaction) and iodine (detected with starch) a determination of these elements will be necessary. Details of the application of each test are given.
A. O. JONES

4744. **Separation and determination of methacrylamide and methacrylic acid in the reaction product of methyl methacrylate monomer.** Motohisa Furusawa, Tsugio Takeuchi and Ichiro Inoue (Fac. of Engng, Yamanashi Univ., Miotoyanagi-cho, Kofu). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1960, **63** (11), 1949–1952.—Methacrylamide (**I**) is hydrolysed in 2N to 3·4N-H_2SO_4 containing $CuSO_4$ as polymerisation inhibitor and the methacrylic acid (**II**) formed is distilled together with that originally present and water. The total **II** is titrated alkalimetrically in the presence of formaldehyde to eliminate the effect of HCN derived from

acetone cyanohydrin). The interference of α-hydroxyisobutyric acid and α-mercaptoisobutyric acid is eliminated by re-distillation. The amount of **I** is calculated from the difference between the sum and the **II** content measured by direct distillation from a neutral soln. in the presence of tartaric acid and Na_2SO_4 (*cf.* Takeuchi *et al.*, *Anal. Abstr.*, 1959, **6**, 1841). *Procedure*—To the aq. soln. containing <200 mg of **I** plus **II**, add $CuSO_4$ (1 g), H_2SO_4 (5M) (50 ml) and water to 100 ml, and heat under reflux for 60 min. Add water (50 ml), Na_2SO_4 (35 g), H_2SO_4 (5M) (5 ml), water (75 ml) and a few pieces of tin, distil and collect 120 ml of the distillate. Re-distil again, collecting 120 ml of distillate, to which add neutral formaldehyde soln. (20%) (10 ml) and titrate with 0·1M-NaOH. K. SAITO

4745. **Determination of copolymer composition by infra-red analysis. Poly(vinyl acetate) - poly(methyl acrylate).** S. N. Chinai and R. H. Campbell (Monsanto Chemical Co., Boston, Mass., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 577–579.—The method is based on the fact that the i.r. absorption spectra of methyl esters between 7·7 and 9·0 μ are different from those of esters derived from larger alcoholic groups. The spectrum of poly(methyl acrylate) showed max. at 7·9, 8·35 and 8·55 μ, while that of poly(vinyl acetate) showed one very strong max. at 8·0 μ. Application of simultaneous equations of extinction values obtained at 8·0 and 8·55 μ enabled each compound to be measured in the presence of the other. The accuracy is within 2·2% absolute, and the standard deviation is 0·99% for each compound. G. P. COOK

4746. **A new lactic acid - urea method for the quantitive determination of urea - formaldehyde and melamine - formaldehyde resins on fabrics from regenerated cellulose fibres.** F. Kočevar. *Textilrdsch.*, 1961, **16** (3), 109–114.—In the method described, the fabric is boiled under reflux for 1 hr. with lactic acid and urea, the liquid is drained off, and the boiling is repeated for another hour with fresh urea - lactic acid soln. The fabric is then rinsed with hot and cold water until the washings are free from acid, then dried at 105° to constant weight, cooled and weighed. The amount of resin is calculated as the percentage addition to the dry weight of the untreated fabric from the formula— $x = [100(A - a) - Af]/a\%$, where a is the weight of the stripped fabric, A the weight of the dried resin-containing fabric, and f the correction factor (0·7 for cellulosic and 0·5 for rayon fabrics or, if a single lactic acid - urea treatment has been carried out for urea - formaldehyde resins, 0·5 and 0·4, respectively). SHIRLEY INST. ABSTR.

4747. **Infra-red procedure for the qualitative and quantitative identification of rubber and related polymers used in paper products.** C. P. Puchalsky and J. E. Newell. *TAPPI*, 1960, **43** (12), 197A–203A.—The identification is achieved by the comparison of the i.r. absorption spectra of the polymer with given reference spectra. The spectra of 16 resin and rubber polymers, including nitrile rubber and SBR, are shown graphically. The experimental procedure is described. RUBB. ABSTR.

4748. **Differential thermal studies [of propellents] with simultaneous gas-evolution profiles.** W. M. Ayres and E. M. Bens (Res. Dept., U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 568–572.—The differential thermal study of propellents is greatly improved by the addition of a simultaneous and continuous gas-detection system. An inert gas flowing through the system removes gaseous reaction products, which are detected by a thermal-conductivity cell, allowing thermograms with gas profiles to be recorded. Examples indicate the value of this technique as a research tool. C. B. BAINES

4749. **Analysis of explosives in non-aqueous media. Determination of diphenylamine derivatives.** L. Marvillet and J. Tranchant (Service des Poudres, France). *Chim. Anal.*, 1961, **43** (4), 169–173.—A method is described for the determination of diphenylamine (**I**), 2-nitrodiphenylamine (**II**), 2,4-dinitrodiphenylamine (**III**) and *N*-nitrosodiphenylamine (**IV**). *Procedure*—Extract the explosive in a Soxhlet extractor with dichloromethane for 1 day. (*i*) *For* **I**—Evaporate an aliquot of the extract, and dissolve the residue in 50 ml of acetic acid and 40 ml of acetic anhydride. Titrate the mixture potentiometrically with 0·03N-$HClO_4$ in acetic acid with a glass and silver - silver chloride electrode-pair. (*ii*) *For* **II** *and* **III**—Evaporate an aliquot of the extract, and dissolve the residue in 70 ml of neutral dimethylformamide. Titrate the soln. potentiometrically, under N, with 0·1N-tributylmethylammonium hydroxide in isopropyl alcohol. Separate inflections are given on the curve for **II** and **III**. (*iii*) *For* **IV**—Evaporate an aliquot of the extract, and dissolve the residue in 70 ml of acetic acid. Add 15 ml of 0·5% 1-naphthylamine (**V**) soln. in acetic acid and heat, protected from light, for 30 min. on a water bath at 60°. Cool, and determine the excess of **V** with 0·03N-$HClO_4$ in acetic acid. The error is generally within ±2% for all constituents, and the method is rapid and simple. R. A. HENDEY

4750. **Methods for analysis of polyphenyl reactor coolants.** R. T. Keen, R. A. Baxter, L. J. Miller, R. C. Shepard and M. A. Rotheram (Atomics International, Div. of North American Aviation, Inc., Canoga Park, Calif., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. NAA-SR-4356, 1961. 56 pp.—Analytical methods developed for the study of irradiated and un-irradiated polyphenyl reactor coolants are explained in detail. Gas-chromatographic methods are described for the determination of biphenyl, *o*-, *m*- and *p*-terphenyl, benzene, toluene and ethylbenzene in irradiated polyphenyl coolants. Other low-boiling components are also determined collectively by a gas-chromatography method. An u.v. spectroscopic method is given for the determination of triphenylene (a radiolytic decomposition product of terphenyls). A low-voltage mass-spectroscopic technique is described for a "group-type" analysis of the higher-boiling decomposition products of polyphenyl coolants. Masses are assigned to phenyl, alkyl and hydro-derivatives of polyphenyls, triphenylenes and phenanthrenes. Methods are also reported for the determination of gross properties such as high-boiling constituents of coolants, average molecular weight, carbon and hydrogen content, and olefin (unsaturation) content by ozone absorption. NUCL. SCI. ABSTR.

See also Abstracts—**4453**, Redox indicators for titration of quinol. **4455**, Indicators for titration of organic acids. **4631**, Determination of Br^- and SCN^- in developers. **4788**, Gas chromatography

of higher alcohols. **4823**, Determination of piperazine. **4840**, Gas chromatography of C_4 to C_{20} free fatty acids. **4841**, Separation of C_{10} to C_{16} fatty acids. **4848**, Fluorescence spectra of aromatic hydrocarbons. **4849**, Determination of benzo(*a*)pyrene. **4860**, Determination of dithiocarbamates and thiuram disulphides. **4879**, Gas chromatography of lower paraffins. **4884**, **4885**, Gas chromatography of polymers. **4888**, Flame-ionisation detector for hydrocarbons.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

4751. **Chemical determination of trace elements in biological material. XX. Micro-determination of copper in plant ash by controlled-potential electrolysis.** Masaru Suzuki and Katsumi Yamamoto (Chem. Dept., Fac. of Sci., Tohoku Univ., Katahira-cho, Sendai). *Japan Analyst*, 1960, **9** (2), 143–147.—Copper (100 to 600 μg) in plant ash is quant. deposited on platinum wire at $-0{\cdot}130$ V *vs.* the S.C.E. from 0·4N-H_2SO_4 within 60 min., the amount of Cu remaining being <7 μg. The sample ash is dissolved in HCl and centrifuged, the residue is treated with H_2SO_4 and HF, and finally dissolved in H_2SO_4 and combined with the filtrate, which is converted into H_2SO_4 soln. for electrolysis.

K. Saito

4752. **The determination of magnesium in biological materials by atomic absorption spectrophotometry.** J. B. Dawson and F. W. Heaton (Dept. of Med. Phys., Univ. of Leeds, England). *Biochem. J.*, 1961, **80** (1), 99–106.—An instrument suitable for the determination of Mg by this method is described. The method involves passing light containing a high proportion of Mg resonance radiation through a flame. The soln., the Mg content of which is to be determined, is aspirated into the flame, and the light absorbed at 285·213 mμ is compared with the absorption of a standard Mg soln. which is treated similarly. The method is applicable to serum, urine and blood and soln. of the ash from food or faecal matter after treatment with HCl. Other inorganic ions have no significant effect on the determination. The organic constituents present in some samples cause slightly high values for Mg to be obtained. A comparison of the atomic absorption method with the ammonium phosphate method shows that the former is accurate to within 2% of the absolute value.

J. N. Ashley

4753. **Rapid method for determining magnesium in plant material.** E. G. Bradfield (Res. Sta., Long Ashton, Bristol, England). *Analyst*, 1961, **86**, 269–271.—The reagent is an aq. soln. of Titan yellow, standardised spectrophotometrically by a method described, a calculated amount of which is added to specified amounts of water, poly(vinyl alcohol) and glycerol. A compensating soln. is prepared by dissolving 5 g of 1,2-di-(2-aminoethoxy)ethane-NNN′N′-tetra-acetic acid in the minimum amount of 10% NaOH soln., adjusting the pH to $\simeq 7$ with dil. HCl, adding 0·054 g of $AlCl_3.6H_2O$ dissolved in a small amount of water, then 20 ml of triethanolamine and diluting the soln. to 200 ml. The ash of 0·1 g of ground plant material is dissolved in 5 ml of 0·5N-HCl, the soln. is diluted to 10 ml, and 2 ml of the compensating soln. is added. To the liquid in a tube in a water bath at 25° are added 4 ml of Titan yellow reagent and, after mixing, 4 ml of 14% NaOH soln. After 30 min. the extinction of the liquid is measured at 550 mμ and referred to a calibration graph. There is no interference from Ca or PO_4^{3-} and tolerance of Fe, Al, Mn, Zn and Cu up to stated limits is ensured by the ingredients of the compensating soln. Results agree satisfactorily with those obtained by a volumetric method with 8-hydroxyquinoline.

A. O. Jones

4754. **Determination of calcium and magnesium in urine by atomic absorption spectroscopy.** J. B. Willis (C.S.I.R.O. Chem. Res. Lab., Melbourne, Australia). *Anal. Chem.*, 1961, **33** (4), 556–559.—In this determination, the specimens are diluted 5 to 50-fold with a soln. of either $LaCl_3$ or $SrCl_2$. Recoveries of Ca from urine were between 95·5 and 101·5% in the concn. range of 1 to 10 p.p.m. and results also compared well with those of the oxalate - permanganate titration method. Magnesium can also be determined by a similar procedure. The amount of sample required is only 0·1 to 1 ml.

G. P. Cook

4755. **Investigation of Nuclear Fast Red method of Baar for direct spectrophotometric determination of calcium in serum, urine and spinal fluid.** G. R. Kingsley and O. Robnett (Sch. Med., Univ. Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 552–556.—The effects of time, temp., concn. of reagents, and various interfering substances were evaluated to determine the optimum conditions for using Nuclear Fast Red (C.I. Azoic Diazo Component 5). The proposed modifications improved the performance of the original Baar method for Ca (*Anal. Abstr.*, 1958, **5**, 1590). Recoveries of added Ca from serum were 93 to 105% in the range of 1 to 4 mg.

G. P. Cook

4756. **Paper-chromatographic separation and complexometric titration of trace amounts of strontium and calcium in biological material.** P. A. Dumont (Univ. Louvain, Belgium). *Anal. Chem.*, 1961, **33** (4), 565–567.—Samples are burned in a closed atmosphere of oxygen and the residues are dissolved in dil. HNO_3. The Ca and Sr are then separated from each other by ascending paper chromatography, followed by ignition at 410° to 430° of the corresponding spots. The two metals are individually determined by titration with EDTA, with calcein as indicator. The procedure is accurate to within 2% for both metals at the 25×10^{-3}M level, the coeff. of variation being 5%.

G. P. Cook

4757. **Method for measuring zinc in leucocytes and erythrocytes.** R. E. Fredricks, Kouichi R. Tanaka and W. N. Valentine (Univ. California Med. Center, Los Angeles, U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 169–173.—The erythrocytes and leucocytes of venous blood are separated by treatment with cell-sedimenting soln. and centrifuging; Zn is extracted from the cells in the supernatant liquid (leucocytes) and sediment (erythrocytes) after treatment with trichloroacetic acid and centrifuging under prescribed conditions. The Zn is determined spectrophotometrically in a dithizone - CCl_4 extract at 520 mμ in 1-cm cells against duplicate Zn-free

H_2O blanks treated identically, and duplicate standards (2 to 3 μg of Zn). The normal range for human blood (μg of Zn per 10^{10} cells) is 9·3 to 15·5 for erythrocytes, and 56·8 to 168 for leucocytes.

M. A. ELLIS

4758. **Butanol extraction as an addition to the [serum] iodine determination method of Spitzy, Reese and Skrube.** R. Kotzaurek (Med. Univ.-klinik, Wien, Austria). *Klin. Wochschr.*, 1960, **38** (19), 995–997.—Serum (0·5 ml), 10% H_2SO_4 (pH 2 to 3) (0·1 ml) and n-butanol (5 ml) are shaken in a stoppered centrifuge tube for 3 min., then centrifuged for 10 min. at 2000 r.p.m., and the supernatant liquid is transferred to a 25-ml separating-funnel. The protein ppt. is treated with a further 2·5 ml of n-butanol, shaken and centrifuged, and the supernatant fluid is added to the first butanol wash. Blau's reagent (5% of Na_2CO_3 in 10% NaOH soln.) (10 ml) is added to the combined butanolic extracts and the mixture is shaken for 5 min. and then set aside for 6 hr. The butanol phase is separated and shaken twice with a further 10 ml of Blau's reagent, 3 hr. being left between each extraction. Simultaneously two standards are set up, with 0·1 ml of 10% H_2SO_4 and 7·5 ml of n-butanol, each being treated three times with Blau's reagent in the same way as the serum sample. The combined butanolic extracts are then placed in the digestion flask of the iodine-determination apparatus of Spitzy *et al.* (*Anal. Abstr.*, 1959, **6**, 658), and evaporated to dryness at 200° in a drying oven. The dry residue is then treated as in the original method of Spitzy *et al.* (*loc. cit*). This method has been applied to a series of 51 patients, some of whom had received previous medication with various iodine-containing compounds. It is shown that these compounds affect the values of the total serum iodine and the serum protein-bound iodine, but have a negligible effect on the value of the butanol-extractable iodine.

D. B. PALMER

4759. **The determination of iodine-131 in vegetation, milk, thyroid gland and natural water.** Tech. Manager (Chem.), Windscale (U.K.A.E.A., Risley, Lancs., England). U.K.A.E.A. PG. Report 204(W), 1961. 11 pp.—Suitable pre-treatments are described for converting the ^{131}I into alkali iodide. Free iodine is then liberated by the addition of hydroxylamine, $NaNO_2$ and HNO_3 and is extracted into CCl_4. The iodine is then back-extracted into aq. SO_2 soln. After removal of SO_2, the I^- are pptd. as AgI, the ppt. is transferred, as a slurry in 0·1M-HNO_3, to a stainless-steel counting tray, evaporated to dryness, and weighed, and its β-activity measured. Directions are given for calibrating the counter efficiency with ^{90}Sr - ^{90}Y.

G. RUSSELL

4760. **Determination of acid-soluble phosphoric fractions in human liver. I. Technique and observations on normal subjects.** M. Bistocchi and F. Orlandi (Ist. Chim. Biol. e Clin. Med., Univ. Perugia, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1961, **37** (7), 307–310.—Biopsy samples of human liver were taken from individuals maintained on controlled diets for 48 to 72 hr. before biopsy. Samples were taken in the morning, 12 to 13 hr. after the last meal. The sample (15 to 25 mg), washed and dried between filter-paper, was homogenised at 0° with 5% trichloroacetic acid soln. (0·2 ml) then centrifuged. An aliquot of the supernatant liquid (120 to 150 μl) was submitted to descending chromatography on Whatman No. 1 paper (previously washed with 0·2% EDTA at pH 8·5) with n-propanol - trichloroacetic acid - conc. aq. NH_3 - H_2O (75:5:1:20) for ≃14 hr. at 18° to 20°. Adenosine compounds were located on the dried chromatogram in u.v. light and the various phosphoric fractions were stained by a modification of Hanes and Isherwood's procedure (*J. Biol. Chem.*, 1951, **193**, 405). The various substances were identified by their R_F values—(*i*) adenosine 5′-tri-, di- and mono-phosphoric acids, located in u.v. light, have R_P values of 0·05, 0·12 and 0·50, respectively; (*ii*) inorganic P is readily distinguished either by its R_F value (0·67) or by the formation of yellow molybdophosphate before hydrolysis of other substances; (*iii*) hexose phosphates have R_F values between 0·20 and 0·35; (*iv*) triose phosphates have R_F values between 0·52 and 0·60. After identification the spots were cut out and wet-ashed, and the P was determined by the method of Strickland *et al.* (*Biochem. J.*, 1956, **62**, 512). The method is sensitive to 0·5 μg of P and recovery from the chromatograms is 97%.

J. I. M. JONES

4761. **Comparative study of colorimetric determination of phosphorus. IV. Determination of orthophosphate in the presence of phosphoric esters (new methods).** J. L. Delsal and H. Manhouri (Inst. Razi, Teheran). *Arch. Inst. Hessarek*, 1960, **12**, 43–61.—Four modifications of the determination of orthophosphate or phosphatases in the presence of phosphoric esters are discussed, with special reference to the effect of pH and the presence of cysteine, glutathione, Cu, trichloroacetic acid, $HClO_4$, $(NH_4)_2SO_4$ and adenosine triphosphate (**I**) on the maximum extinction and the stability of the colour. The first method is that of Berenblum and Chain (*Biochem. J.*, 1938, **32**, 295), but carried out at pH 2·5 [to reduce the effect of $(NH_4)_2SO_4$], with $(NH_4)_2MoO_4$, H_2SO_4, butanol and $SnCl_2$, and a 735-mμ filter. The blank must contain **I** when it is present in the sample. In the second method, carried out at pH 4 and with a 735-mμ filter, the extraction is omitted. Stannous chloride is dissolved in acetic acid and an acetate buffer is used. Formaldehyde must be added when cysteine and glutathione are present. In the third method, 1-amino-2-naphthol-4-sulphonic acid is used in the presence of Cu at pH 4 with an acetate buffer and an 880-mμ filter. The rate of reaction and intensity of colour are affected by the Cu. Trichloroacetic acid stabilises the colour, and its use is necessary in the presence of $(NH_4)_2SO_4$ and $HClO_4$, but a waiting period of 15 min. is required. Cysteine requires centrifugation. In the fourth method, *p*-methylaminophenol sulphate is used with an acetate buffer, Na_2SO_3 and 5×10^{-3}M-$CuSO_4$, with a 2-min. waiting period and an 880-mμ filter at pH 4. Beer's law applies for 4 to 20 μg of P. This method is more sensitive than the others, is less affected by the presence of cysteine, glutathione and **I**, and the colour stability is greater. The *p*-methylaminophenol sulphate can be replaced by quinol or 2,4-diaminophenol hydrochloride.

CHEM. ABSTR.

4762. **Method for determining the oxygen-18 content of orthophosphate or water.** A. B. Falcone (Metabol. Res. Lab., Vet. Admin. Hospital, Madison, Wis., U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 147–151.—The procedure previously described (Cohn, *J. Biol. Chem.*, 1949, **180**, 771; Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, **60**, 679), in which the orthophosphate is pyrolysed to metaphosphate and water, the water formed is equilibrated with a

known amount of CO_2, and the 46 to 44 ratio of the CO_2 is then determined mass-spectrometrically, has been rendered more rapid by the use of a high-voltage discharge to accelerate the equilibration. As little as 2 mg of KH_2PO_4 can be analysed. The apparatus and method of calculation are described.
R. E. E.

4763. **Determination of erythromycin in blood serum and urine by diffusion into agar.** N. A. Vakulenko (All-Union Sci. Res. Inst. of Antibiotics). *Antibiotiki*, 1961, **6** (4), 315–318.—Erythromycin (**I**) in blood serum and urine is determined by the cup-plate method with a medium containing 1·5% of agar in a tryptic fibrin hydrolysate adjusted to 28 to 30 mg of amino-N per 100 ml and pH 7·8 to 8, with the test organism *B. mycoides* HB-2. If the concn. of **I** is >0·8 unit per ml, the sample is diluted (1:2) with phosphate buffer soln. of pH 7·8 to 8. The minimum determinable concn. of **I** is 0·2 unit per ml, and the accuracy is ±10%.
C. D. Kopkin

4764. **Estimation of phenothiazines using chemically impregnated paper strips.** J. H. Heyman, B. Bayne and S. Merlis (Central Islip State Hosp., N.Y., U.S.A.). *Amer. J. Psychiat.*, 1960, **116**, 1108–1109.—Strips (0·5 in. to 1 in. × 7 in.) of Whatman 3MM paper are impregnated with 0·001M-$Hg(NO_3)_2$, 0·001M-$UO_2(NO_3)_2$, or 0·001M-$Hg(NO_3)_2$ plus 0·5M-$(NH_4)_2S_2O_8$. The strips can be used while wet and are stable for only a few days when dry. For the test, apply 1 drop of urine, 1 drop of 3% H_2O_2 soln. and 1 drop of conc. HCl. Omit H_2O_2 when using $(NH_4)_2S_2O_8$-treated strips. Positive reactions range through pinks, mauves and browns according to the drug. False positive results were obtained in the presence of increased bile pigments. The results generally agree with those obtained with the Forrest universal test (Forrest and Forrest, *Anal. Abstr.*, 1961, **8**, 1147) and the Forrest test for piperazine-linked phenothiazines (Forrest *et al.*, *Amer. J. Psychiat.*, 1959, **116**, 549).
Chem. Abstr.

4765. **Rapid urine colour test for imipramine (Tofranil).** I. S. Forrest and F. M. Forrest (V. A. Hosp., Brockton, Mass., U.S.A.). *Amer. J. Psychiat.*, 1960, **116**, 840–841.—To 1 ml of urine add 1 ml of a mixture of equal parts of 0·2% $K_2Cr_2O_7$ sc'n., 30% (v/v) H_2SO_4, 50% (v/v) HNO_3 and 20% $HClO_4$; mix, and observe the colour. With daily doses of 25 to 250 mg of imipramine, the colour ranges from pale olive to deep emerald green, lasting from 15 to 25 sec. to 60 sec., respectively. In 300 tests, there were no false positive or negative reactions. Control urines give a pale yellow, ochre, or orange colour. With phenothiazine drugs, the colour is a transient pink, purple or violet. If imipramine is administered with a phenothiazine drug, the green colour appears after the phenothiazine colour has faded.
Chem. Abstr.

4766. **Rapid colour test for imipramine (Tofranil): supplementary report with colour chart.** I. S. Forrest, F. M. Forrest and A. S. Mason (V. A. Hosp., Brockton, Mass., U.S.A.). *Amer. J. Psychiat.*, 1960, **116**, 1021–1022.—With the test as originally described (Forrest and Forrest, *Anal. Abstr.*, 1961, **8**, 4765), the phenothiazine drugs do not interfere provided that their daily dose does not exceed 500 mg and is not more than 5 times the dose of imipramine. When the dose is 400 mg or more, modify the test by using 1 ml of urine plus 2 ml of reagent. 4-Aminosalicylic acid in large doses has given delayed trace reactions. Phenylketonuric urines give negative reactions.
Chem. Abstr.

4767. **A rapid urine colour test for thioridazine (Melleril).** I. S. Forrest, F. M. Forrest and A. S. Mason (V. A. Hosp., Brockton, Mass., U.S.A.). *Amer. J. Psychiat.*, 1960, **116**, 928–929.—To 1 ml of urine add 1 ml of a mixture of 2 parts of 5% $FeCl_3$ soln. and 98 parts of 30% (v/v) H_2SO_4, mix, and observe the colour after 20 to 30 sec. The colour ranges from a pale, purplish pink for daily doses below 150 mg of thioridazine, through more intense purple and violet to blue for an intake of 1 g daily. In over 1800 tests there were no false negative reactions. Low values were obtained with very dil. urines. In 500 tests, there were 2 false positive reactions, apparently due to 4-aminosalicylic acid medication. Other phenothiazine drugs given simultaneously, or recently discontinued, interfere. Phenylketonuric urines may give slight positive results.
Chem. Abstr.

4768. **Ultra-micro method for the determination of urea nitrogen in blood serum.** G. V. de Nieves and R. L. Pike (Dept. of Foods and Nutrition, Pennsylvania State Univ., University Park, U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 174–177.—Archibald's method (*J. Biol. Chem.*, 1944, **156**, 121; *Ibid.*, 1945, **157**, 507) is adapted for use with 5 µl of serum. *Procedure*—Prepare a calibration curve from aq. standards (in triplicate) containing 300, 200 and 100 µg of urea-N per ml, by the addition of 5% trichloroacetic acid soln. (10·5 µl). Centrifuge for 15 to 20 min. To the supernatant liquid (5·1 µl) add H_2O (48 µl), H_2SO_4 - H_3PO_4 - H_2O (1:3:1) (48 µl) and 4% ethanolic α-hydroxyiminopropiophenone soln. (10·1 µl). Place in a boiling-water bath for 1 hr., excluding light, set aside for 15 min. in water at room temp. and measure the extinction at 540 mµ in a 2·5-mm cell against a reagent blank. Treat serum samples similarly. Beer's law is obeyed over the range 100 to 400 µg of urea-N per ml. The coeff. of variation (43 sets of triplicate determinations) was ±0·51% with a mean recovery of 97·5%, over the range from 1·56 to 12·50 µg of urea-N per ml added to rat serum.
M. A. Ellis

4769. **Simple spectrophotometric method for the determination of blood sugar by phenylhydrazine hydrochloride.** M. Aghdashi. *Arch. Inst. Hessarek*, 1960, **12**, 119–126.—The method described is a modification of that of Wahba *et al.* (*Anal. Abstr.*, 1957, **4**, 608). Protein-free filtrate (1 ml ≡ 0·1 ml of blood) and 9 ml of phenylhydrazine reagent (8 g of phenylhydrazine hydrochloride and 20 g of $Na_2S_2O_5$ are dissolved in 100 ml of H_2O, and 900 ml of aldehyde-free acetic acid is added; the soln. is refrigerated overnight, filtered, and stored in the refrigerator) were heated for 30 min. on a boiling-water bath. After cooling, the soln. was diluted to 10 ml and the extinction determined at 400 mµ. Beer's law was obeyed for concn. up to 120 µg of glucose per ml when a Beckman DU spectrophotometer was used. The method was applicable to Folin - Wu, Somogyi and $CdSO_4$ - NaOH deproteinised soln. The results averaged about 2% lower than the anthrone and 4% lower than the copper reduction methods. Ascorbic acid had a colour yield that was 10% of that of glucose on a weight basis, but the concn. of ascorbic acid in blood was not high enough to interfere.
Chem. Abstr.

4770. **Estimation of sugars in paper chromatograms and paper electrochromatograms sprayed with ammonium molybdate.** H. El Khadem and W. Girgis (Chem. Dept., Alexandria Univ., Egypt). *Anal. Chem.*, 1961, **33** (4), 645–646.—Improved results are obtained when the colour of the reducing-sugar spots that have been revealed with 10% aq. ammonium molybdate is developed, for determination, with an ammonium molybdate reagent that has been made up with dil. H_2SO_4 instead of the usual HCl. G. P. Cook

4771. **Selective determination of sugars manifesting enediol isomerism by means of reaction with tetrazolium.** G. Avigad, R. Zelikson and S. Hestrin (Dept. of Biol. Chem., Hebrew Univ., Jerusalem, Israel). *Biochem. J.*, 1961, **80** (1), 57–61.—Tetrazolium salts in aq. soln. at pH 12·4 are readily reduced at 37° by sugars that can exhibit enediol isomerism. This is the basis of a method for the determination of 6-R-fructose and fructose in the presence of 1-R-fructose, and of aldoses in the presence of 2-deoxyaldoses. Conditions are established under which the rate of the reduction of tetrazolium to formazan is a linear function of the concn. of the sugar over a wide range of concentration. The use of 2,5-diphenyl-3-(4-styrylphenyl)tetrazolium in this reaction allows smaller amounts of the sugar to be determined than is possible when 2,3,5-triphenyltetrazolium is used. The formazan formed after a specified time is dissolved in acidified methanol or propanol, and the extinction is determined spectrophotometrically at 485 mμ with triphenylformazan, and at 510 mμ with the diphenylstyrylphenylformazan. The presence of methanol, ethanol or isopropyl alcohol in the reaction mixture during the reduction markedly increases the rate of formation of the formazan, and almost completely abolishes the selectivity of the reaction as between 6-R- and 1-R-fructose. J. N. Ashley

4772. **Micro-determination of dihydroxyacetone in biological fluids.** M. U. Tsao and E. L. Schwartz (Univ. of Michigan Med. Sch., Ann Arbor, U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 107–113.—The method is based on the colour formed in alkaline solution by the osazone of dihydroxyacetone. Blood (1·5 ml) or homogenised tissue is deproteinised with sulphosalicylic acid soln., incubated with glucose oxidase soln. to remove glucose and treated with 2,4-dinitrophenylhydrazine. The excess of reagent is removed by reaction with pyruvic acid and partition in benzene - $NaHCO_3$ soln. After removal of the benzene, the colour is developed with ethanolic NaOH and read at 586 mμ. The method can be applied to urine with slight modifications. Standards of similar concn. ranges are treated concurrently. The determinable minimum is 5 μg of dihydroxyacetone; most monosaccharides do not interfere. For three blood samples (six replicates), the standard deviations were 0·6, 1·5 and 1·3, and, for four urine samples, 3·0, 2·2, 2·2 and 1·3 μg per ml, respectively. M. A. Ellis

4773. **Estimation of 4-hydroxy-3-methoxymandelic acid in urine.** M. Sandler and C. R. J. Ruthven (Bernhard Baron Memor. Res. Lab., Queen Charlotte's Maternity Hosp., London). *Biochem. J.*, 1961, **80** (1), 78–82.—This acid is a major metabolite of adrenaline and noradrenaline, and the assay is a useful index of catecholamine metabolism. The method depends on adsorption of the acid on a column of the anion-exchange resin Dowex AG1-X2; after elution and extraction of the acid into dil. acid, the soln. is autoclaved whereby the organic acid is converted into vanillin, which is then determined spectrophotometrically. *p*-Acetamidophenol, but not salicylic acid, interferes with the determination. The accuracy and specificity are sufficiently high to make the method suitable for following physiological fluctuations in the low concn. of 4-hydroxy-3-methoxymandelic acid excreted in the urine of normal persons. Mean recoveries of the acid from urine are 73 ± 6·6%. The method also helps in the clinical diagnosis of the catecholamine-secreting tumour, phaeochromocytoma. J. N. Ashley

4774. **Silica-gel chromatography of organic acids from plant tissue.** H. G. Wager and F. A. Isherwood (Low Temp. Res. Sta., Cambridge, England). *Analyst*, 1961, **86**, 260–266.—The sample (20 g) is extracted by boiling with ethanol. The insol. residue is homogenised with 70% aq. ethanol and filtered, and the solid matter is repeatedly extracted (each time for 1 to 2 hr.) with aq. ethanol. The combined extracts are evaporated with $MgCO_3$ to a syrup, which is extracted repeatedly with light petroleum to remove chlorophyll, carotenoids and lipids. It is then diluted, evaporated to a paste, redissolved in water (5 ml), made into a slurry with $CHCl_3$ and purified, after acidification, by passage through a silica-gel column, elution being continued with a 50% (v/v) soln. of butanol in $CHCl_3$. An extract of the eluate with aq. NaOH soln. is evaporated, the residue, dissolved in water, is transferred to an assembly for chromatography with silica-gel columns in which it is acidified, and the organic acids are separated by gradient elution with $CHCl_3$ containing increasing amounts of butanol. The fractions (≃150), collected automatically, are titrated with 0·01N-NaOH and the results are plotted against fraction numbers. The composition corresponding to each of the peaks thus obtained is determined by two-dimensional paper chromatography. About 25 acids were thus separated from a 25-g sample of green peas. A. O. Jones

4775. **Determination of gibberellic acid by paper chromatography.** M. Podojil and V. Ševčík (Československ. Akad. Věd, Prague). *Folia Microbiol., Prague*, 1960, **5**, 192–197 (in English).—The method is based on descending chromatography with butyl acetate - H_2O. The sensitivity is 5 μg, and the error is ±10%. Adjust a sample of the fermentation medium to pH 2·5 to 3, extract with butanol, apply 0·05 ml of the organic layer to paper, and, after equilibration, develop for 7 hr. with butyl acetate saturated with H_2O, allowing the solvent to drip off the bottom of the sheet. Detect by spraying with a 3% soln. of H_2SO_4 in methanol, dry, and evaluate the area of the spots showing u.v. fluorescence. Read the concn. from a calibration curve. Chem. Abstr.

4776. **Determination of usnic acid in lichens.** H. Gertig (Pharmacog. Garden, Med. Acad., Poznań, Poland). *Acta Polon. Pharm.*, 1961, **18** (1), 57–66.—*Procedure*—Extract 1 g of powdered sample with $CHCl_3$ (10 ml) by heating under reflux for 45 min., cool and filter off 5 ml of the extract. Apply 0·1 to 0·2 ml (≃0·01 to 0·02 g of sample) to 45-cm strips of Whatman No. 1 paper, previously washed with H_2O. Develop the chromatogram with n-butanol - acetone - H_2O (5:1:2) for 14 hr., by the descending technique. Locate the spots of usnic acid in u.v. light (R_F ≃0·85, dark-violet

fluorescence), cut out the spots and extract them with $CHCl_3$ (2 × 5 ml) by boiling under reflux. Evaporate the soln. to 2 ml, add 0·5 ml of a mixture of 1% methanolic uranyl acetate and 1% methanolic $FeCl_3$ (1:1), and measure the extinction in a Pulfrich photometer with a S47 filter. Refer the result to a calibration curve. The accuracy is ±3·7%. B. K.

4777. **Improved method for the rapid determination of porphyrins [in urine].** R. Hoschek. *Zbl. Arbeitsmed. u. Arbeitsschutz*, 1960, **10**, 134–137.—Porphyrins were detected by the addition of 4 drops of 2% *p*-dimethylaminobenzaldehyde in 20% HCl to 5 ml of urine. The mixture was subjected to u.v. irradiation through a cobalt filter and the resulting fluorescence examined through a red filter. Porphyrin-free urine gave a yellow fluorescence not detectable through the red filter. The red fluorescence of porphyrins was easily detectable at concn. >5 μg per 100 ml. The method may be made more quantitative by comparisons with photographic plates carrying drops of various concn. of Rhodamine B (C.I. Basic Violet 10) or haematoporphyrin in acetic acid. Addition of 5 drops of H_2O_2 converts porphobilinogen to porphyrin and enables the former to be determined by difference. The method is rapid, simple and inexpensive, but does not differentiate uroporphyrin from coproporphyrin. CHEM. ABSTR.

4778. **Study of the Soret band: a screening method for urinary porphyrins.** N. Zenker (Mount Zion Hospital, San Francisco, Calif., U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 89–99.—The characteristic u.v. absorption (Soret) bands due to uroporphyrin (**I**) and coproporphyrin (**II**) are used for the quant. determination of **I** and of total porphyrins. The behaviour of **I** in the presence of **II** is studied, and conditions are established for the determination of **I** and of total porphyrins in urine, without preliminary separation, by means of a correction factor. A comparison is made between the proposed method, an extraction method, and the spectrophotometric method of Schlenker and Kitchell (*Amer. J. Clin. Path.*, 1958, **29**, 593). M. A. ELLIS

4779. **Separation of coproporphyrin and protoporphyrin by extraction.** V. Holeček (Inst. for Hyg. and Occupational Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (4), 1187–1194 (in German).—The step-wise extraction of coproporphyrin (**I**) and protoporphyrin (**II**) with ethyl ether from 0·07N- and 2·0N-HCl is described. Exhaustive extraction results in the decomposition of unstable **II** and therefore a single extraction is proposed, using an empirical factor because of the difference in partition coefficients. In the presence of bile, the yield of **I** is 95·3 ± 2·0% and that of **II** is 92·5 ± 2·4%. The advantages of extraction from dilute soln. are pointed out. R. PRESSER

4780. **Micro-method for the fractionation of lipids by silicic acid chromatography.** E. W. Lis, J. Tinoco and R. Okey (Univ. California, Berkeley, U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 100–106.—A micromethod is described for the separation of (*i*) cholesteryl esters, (*ii*) triglycerides, (*iii*) free cholesterol, mono- and di-glycerides, and (*iv*) phospholipids in 1 to 10-mg samples of mixed lipids from plasma. Silicic acid is used in the column (8 mm × 125 mm), and the named fractions are obtained by successive elution with (*a*), 1% ethyl ether (**I**) in light petroleum (**II**); (*b*), 4% of **I**, in **II**; (*c*), 50% of **I**, in **II**; and (*d*) absolute methanol. The fractions are further separated by gas-liquid chromatography for the determination of fatty acids. Recoveries of 90% are claimed. M. A. ELLIS

4781. **Chromatographic methods for the study of amines from biological material.** K. Blau (Biochem. Dept., King's Coll., Strand, London, England). *Biochem. J.*, 1961, **80** (1), 193–200.—Biological fluids and extracts are treated with the ion-exchange resin De-Acidite FFX so as to obtain a fraction which consists mainly of amines. The resolution of this fraction is then achieved by means of buffered columns of the weakly acid resin Zeo-Karb 226. The methods, which are not applicable to amino-acids, avoid extreme conditions of temp. and pH. The amines are isolated as hydrochlorides, and the methods are illustrated with reference to the analysis of the amines in urine. J. N. ASHLEY

4782. **Determination of adrenalines.** A. Jörg and M. Büchner (Krankenhaus Dresden-Friedrichstadt, Germany). *Z. ges. inn. Med.*, 1960, **15**, 354–357.—A modification of the method of von Euler and Floding (*Scand. J. Clin. Lab. Invest.*, 1956, **8**, 288) is described. Adsorption of catecholamines on alumina was improved by using alkali-free alumina that had been heated for 3 hr. at 400°. *Procedure for urine*—After being filtered and acidified with 6N-HCl to pH 1·6, one-tenth of a 24-hr. urine specimen was heated on a boiling-water bath for 15 min. The cooled sample was mixed with 30 ml of 0·2M-Na acetate buffer, pH 8·5, and the mixture brought to pH 8·5 by adding 25% Na_2CO_3 soln. It was then passed through a column containing 2·5 g of alumina that had been washed with the same buffer. The column was washed again with 10 ml of buffer and with 50 ml of H_2O. Catecholamines were eluted with 20 ml of 0·25N-H_2SO_4. A 1-ml aliquot of eluate, 1 ml of M-Na acetate buffer (pH 6·3) and 0·1 ml of 0·25% $K_3Fe(CN)_6$ soln. were mixed, shaken, and allowed to stand for 2 min., then 1 ml of freshly prepared Na ascorbate soln. (1 vol. of 2% ascorbic acid soln. and 9 vol. of 5N-NaOH) was added. The mixture was diluted to 10 ml with H_2O and centrifuged, and the fluorescence of the supernatant liquid was measured as previously described. Adrenaline was used to prepare a standard curve. CHEM. ABSTR.

4783. **Improved technique for the fluorimetric estimation of catecholamines.** U. S. von Euler and F. Lishajko (Physiol. Dept., Karolinska Inst., Stockholm). *Acta Physiol. Scand.*, 1961, **51** (4), 348–356.—The trihydroxyindole method of Lund (*Acta Pharmacol.*, 1949, **5**, 231) was modified by addition of a small amount of ethylenediamine (**I**) to the ascorbic acid - alkali reagent. **I** (0·2 ml) is added to 20% NaOH soln. (9 ml), followed by 1 ml of 2% ascorbic acid soln. The new reagent gives improved stability of the final fluorescent soln., and lower readings of the blanks. Addition of **I** results in an increased fluorescence derived from noradrenaline. That from adrenaline, however, is unchanged. Optimum fluorescence is obtained when the vol. of reagent exceeds the vol. of the sample (which should be less than 3 ml) by 1 ml. At pH 3, urine stored at room temp. for more than 2 weeks showed no significant change in free catecholamine content. At pH values below 1, however, there was a considerable increase in free noradrenaline from readily hydrolysable conjugates. D. G. Moss

4784. **Determination of catecholamines in urine.** V. V. Men'shikov (Hospital Therapeutic Clinic, Sechenov Med. Inst.). *Lab. Delo*, 1961, **7** (4), 18–21.—To determine catecholamines (adrenaline and noradrenaline) in urine, collect the sample in a vessel containing 5 to 10 ml of 2N-H_2SO_4 for each 100 ml of sample. To 25 ml of the soln. add 0·5 g of EDTA, and N-NaOH dropwise to a pH of 8·3 to 8·5, then pass the soln. through 1 g of Al_2O_3 (Brockmann). Wash the column with 10 to 15 ml of water, and elute the adsorbed catecholamines with 10 ml of 0·25N-acetic acid. Make the filtrate slightly alkaline with M-Na_2PO_4, and take 2-ml portions into each of three tubes. To the first add 1 ml of acetate buffer soln. (pH 4·6), then 5 drops of 0·01N-iodine, and after 30 sec. add 2 drops of 0·1N-$Na_2S_2O_3$. To the second tube add 0·5 ml of 50% Na acetate soln. (pH 7·2), and then iodine and $Na_2S_2O_3$ as with the first tube. After 3 to 5 min. add to all three tubes 5 drops of freshly prepared 1% ascorbic acid soln. and 3 drops of 30% NaOH soln. and dilute to 10 ml. Measure the intensity of fluorescence in a fluorimeter through a blue and a yellow-green filter. The difference of readings between the first and the third tubes corresponds to the adrenaline content, and the difference between the second and the third to the noradrenaline content. The sensitivity of the method is 10^{-9} g of substance per ml. When samples of 0·05 to 0·25 μg of the catecholamines were added to 25 ml of urine, the recovery was 70 to 110%.

C. D. KOPKIN

4785. **Uptake of pyrithiamine by tissue of rats. [Determination of pyrithiamine.]** G. Rindi and V. Perri (Inst. of Human Physiol., Univ., Pavia, Italy). *Biochem. J.*, 1961, **80** (1), 214–216.—The determination, which is described in detail, depends on extraction of the pyrithiamine, destruction of any thiamine which may be present, and conversion of the pyrithiamine into a fluorescent product by oxidation with alkaline $K_3Fe(CN)_6$. This product is extracted with isobutyl alcohol, and the fluorescence is measured in a model A Farrand microfluorimeter, and compared with that of a quinine standard. The amounts of pyrithiamine are ascertained from a standard graph, which is linear over the range 0 to 9 μg. For the determination of phosphorylated pyrithiamine, the extract is treated with acid phosphatase and the determination is then repeated. This gives the total pyrithiamine, and the difference between the two results gives the phosphorylated derivative.

J. N. ASHLEY

4786. **Paper-chromatographic separation of amino-acids. A solvent to replace phenol.** M. Mizell and S. B. Simpson (Dept. of Zoology, Tulane Univ., New Orleans, La., U.S.A.). *J. Chromatography*, 1961, **5** (2), 157–160 (in English).—Phenol has a number of disadvantages as a solvent for the separation of amino-acids by paper chromatography. It has been found that the system n-butanol - butanone - water (2:2:1) in an atmosphere satd. with cyclohexylamine is more convenient and reliable than systems containing phenol, and gives good separations of the common amino-acids. Twenty-four amino-acids have been separated by two-dimensional chromatography, with n-butanol - acetic acid - water (25:6:25) as the first solvent and the n-butanol - butanone - water system as the second. The use of cyclohexylamine modifies the colours obtained by spraying with ninhydrin, and assists in the identification of the spots.

R. M. ROWLEY

4787. **Quantitative determination of free and bound amino-acids in blood by ion-exchange elution chromatography.** W. Gerok (Med. Univ.-klinik, Marburg a.d. Lahn, Germany). *Klin. Wochschr.*, 1960, **38** (23), 1212–1215.—To 18 ml of serum was added an equal vol. of 20% (w/v) trichloroacetic acid, and after the protein ppt. had been separated by centrifugation the supernatant fluid was removed by decantation, and filtered. The filtrate (32 ml) was extracted several times with ethyl ether and the aq. phase was evaporated to dryness at 60° to 70° at a pressure of 14 torr, with a rotary drier. The residue was dissolved in 4 ml of citrate buffer (pH 2·2) and a 0·75 to 1·0-ml aliquot (≡ 3 to 4 ml of serum) was used for chromatographic analysis. A second portion (2 ml) of the citrate buffer soln. of the residue was hydrolysed by heating under reflux with 20 ml of 6N-HCl for 6 hr., then evaporated to dryness. The residue was extracted several times with water and the extract was evaporated to dryness, this residue being dissolved in 2 ml of citrate buffer. A 0·75 to 1·0-ml aliquot of this soln. was used for the chromatographic separation. Each mixture of amino-acids was separated on a column of Amberlite CG-120 Type III by the elution method (Moore and Stein, *J. Biol. Chem.*, 1951, **192**, 663; Moore *et al.*, *Anal. Chem.*, 1958, **30**, 1185; Spackman *et al.*, *Ibid.*, 1958, **30**, 1190), and the concn. of amino-acids in each eluate was determined by means of the automatic extinction-reading apparatus of Hannig (*Clin. Chim. Acta*, 1959, **4**, 51). Twenty amino-acids, with the exception of serine and threonine, were determined quantitatively before and after hydrolysis. It is shown that hydrolysis causes a significant increase in concn. of glutamic acid, asparagine, glycine and phenylalanine, all other acids showing no significent change.

D. B. PALMER

4788. **The formation of higher alcohols in the fermentation of amino-acids by yeast. Determination of alcohols by gas chromatography.** Kiyoshi Yoshizawa, Toshiro Furukawa, Makoto Tadenuma and Masakazu Yamada. *Agric. Biol. Chem., Japan*, 1961, **25** (4), 326–332.—Higher alcohols formed during the fermentation by saké yeast and by brewer's yeast of a 10% sucrose soln. containing different sources of N, mineral salts and vitamins were investigated. After distillation through a 50-cm Widmer column the fraction distilling between 79° and 100° was analysed by gas chromatography on columns of dioctyl phthalate (2·5 metres, 105°) or glycerol (8 metres, 75°) with He as carrier gas at 82 and 62 ml per min., respectively. Isoamyl alcohol (**I**) and active amyl alcohol (**II**) were separated only on glycerol. Whatever the nitrogen source the higher-alcohol fraction contained **I** (35 to 50%), **II** (10 to 20%), isobutyl alcohol (20 to 40%) and n-propanol. Saké yeast yielded more higher alcohols than did brewer's yeast. Leucine, isoleucine, valine and α-aminovaleric acid yielded **I**, **II**, isobutyl alcohol and n-butanol, respectively, with either yeast, but alanine gave isobutyl alcohol as the major constituent (saké yeast, 55·5%; brewer's yeast, 39·9%) and α-aminobutyric acid yielded mainly **II** (63%) with the saké yeast, but mainly n-propanol (66%) with brewer's yeast; both yeasts gave **II** as the main alcohol from threonine, and isobutyl alcohol from glycine.

J. R. HUDSON

4789. **Quantitative electrophoresis of serum proteins in the presence of haemoglobin.** C. C. Curtain (Baker Med. Res. Inst., Alfred Hospital, Melbourne, Victoria). *Aust. J. Exp. Biol. Med. Sci.*, 1961, **39** (2), 203–208.—A method is described for correcting serum electrophoresis patterns for the presence of haemoglobin (**I**). The pattern is first photographed in red light at 690 mμ, the cylindrical lens of the Perkin - Elmer model 38A Tiselius instrument is then removed and the direct image of the cell is photographed in green light at 546 mμ. The distribution of **I** along the cell is determined by densitometry of the direct-image negative. Two points of inflection occur in the densitometric curve, the first due to free **I** migrating with the β-globulin, and the second to haptoglobulin-bound **I** migrating with the α_2-globulin. The validity of the method depends on the assumption that free **I** and the **I** in the haptoglobulin complex have the same extinction coeff. at 546 mμ.

E. C. Butterworth

4790. **Copper binding by proteins in alkaline solution.** R. D. Strickland, M. L. Freeman and F. T. Gurule (Veterans Admin. Hosp., Albuquerque, N.M., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 545–552.—The biuret reaction of alkaline copper tartrate with certain proteins was investigated. In all of the proteins studied, except serum globulin, six peptide nitrogens are bound to each copper atom. Methods for determining peptide nitrogen by means of copper binding and for determining proteins by a new titrimetric procedure are proposed.

G. P. Cook

4791. **Determination of haemoglobin in dilute solutions.** A. Martin and M. Zade-Oppen (Univ. Uppsala, Sweden). *Acta Soc. Med. Upsaliensis*, 1960, **65**, 249–257 (in English).—A method is described for measuring the haemoglobin content of fluids containing 1 to 12 mg per 100 ml. To 4 ml of the test soln. is added 0·1 ml of a soln. containing 8 g of $NaNO_2$, 0·208 g of KCN and 4 g of $NaHCO_3$ per 100 ml. The extinction of the cyanmethaemoglobin so formed is measured at 420 mμ after 20 min. The standard deviation was ±1·09%. The extinction of cyanmethaemoglobin was 74·2 at 420 mμ and 7·3 at 540 mμ. In applying the method to plasma, the turbidity of the plasma must be taken into account by making a correction for it or by adding a protein solubiliser.

Chem. Abstr.

4792. **Purification and measurement of microgram amounts of radioactive nucleic acids and proteins from animal cells in tissue culture.** F. M. Kahan (Univ., Toronto, Canada). *Anal. Biochem.*, 1960, **1** (2), 107–126.—Detailed methods are described for the isolation and measurement of microgram amounts of proteins and nucleic acids from animal cells that have incorporated [8-^{14}C]adenine, [1-^{14}C]glycine or [^{32}P]phosphate during tissue culture. The separation of ribonucleic acid from deoxyribonucleic acid, and of the nucleic acids from proteins follows, in principle, the method of Schmidt and Thannhauser (*J. Biol. Chem.*, 1945, **161**, 83) and its modification by Schneider (*Ibid.*, 1945, **161**, 293). In these methods the acid-precipitable fractions are collected on membrane filters (Millipore), and the acid-soluble nucleic acid derivatives are selectively adsorbed on charcoal, which in turn is collected on a similar filter. Each filter is then counted directly. The various steps in the technique, and the factors affecting the method, are fully investigated. A reproducibility of ±90% is reported. This method does not allow the analysis of fewer cells than the conventional methods, but does eliminate repeated centrifuging, prolonged hydrolyses, careful pipettings and quantitative transfer of soln. Also the activity is measured under optimum conditions without the necessity of evaporating the extracts, thus eliminating the self-absorption effect.

D. B. Palmer

4793. **Ultra-micro method for the determination of total serum cholesterol.** I. S. Figueroa and R. L. Pike (Pennsylvania State Univ., University Park, U.S.A.). *Anal. Biochem*, 1960, **1** (2), 103–106.—This method is a modification of the direct method of Zlatkis *et al.* (*J. Lab. Clin. Med.*, 1953, **41**, 486) and requires only 5 μl of serum. The serum proteins are pptd. with glacial acetic acid, and the colour reagent is $FeCl_3$ - conc. H_2SO_4 (1 ml of 10% $FeCl_3$ soln. diluted to 100 ml with conc. H_2SO_4). The reaction takes place at room temp., and the extinction of the reaction product is determined after 30 min. at 560 mμ, with 2·5-mm cells. For measuring the small vol. of serum and reagents, calibrated constriction pipettes are used. Beer's law is obeyed for concn. of cholesterol of 50 to 400 mg per 100 ml, and recoveries of 98·7 to 101·6% are reported. This method is rapid, accurate and reproducible, and is easily performed.

D. B. Palmer

4794. **Turbidimetric determination of total serum cholesterol.** G. R. Kingsley and O. Robnett (Sch. Med., Univ. Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 561–564.—Total serum cholesterol can be determined by measurement of the turbidity produced on addition of sodium ethoxide to the serum. The relationship between turbidity produced and concn. was linear over the range 0 to 420 mg of cholesterol per 100 ml, and the results agreed well with those obtained by other methods.

G. P. Cook

4795. **Turbidimetric determination of cholesterol in blood.** A. F. Krinitskii. *Lab. Delo*, 1961, **7** (4), 27–28.—To 0·2 ml of serum in a tube calibrated at 4 ml add gradually and with stirring 3·8 ml of a mixture of ether and 96% ethanol (1:3) or of acetone and ethanol (1:1), stir for a further 1 or 2 min., and heat to boiling in a water bath (5 to 15 sec.). Rapidly cool in cold water, make up to the original vol., and centrifuge. Take 2 ml of the centrifugate (0·1 ml of serum) into a tube calibrated at 5 ml, add 1 drop of 50% KOH soln. and place the tube in a water bath at 80° to 90°; gradually heat the soln. to boiling and evaporate to 0·5 to 0·8 ml. Cool and neutralise to phenolphthalein with 50% acetic acid, and add 1 ml of digitonin - glycerol reagent (dissolve 1 g of digitonin in 100 ml of ethanol on a water bath, add 100 ml of glycerol and mix). Set aside for 1 to 24 hr., dilute the soln. with 70 to 90% ethanol to 5 ml, mix, and measure the extinction in a 1-cm cell with a blue filter against water. Determine the cholesterol content from a calibration curve. To determine free cholesterol, evaporate 5 ml of the extract (0·25 ml of serum) to 0·5 to 0·8 ml without the addition of KOH, and proceed as described above. The error is within ±5%.

C. D. Kopkin

4796. **Reversed-phase partition chromatography of steroids.** H. E. Carr, jun., and W. J. Reddy (Harvard Med. Sch., Boston, Mass., U.S.A.).

Anal. Biochem., 1961, **2** (2), 152–160.—Cellulose acetate film, 0·15 mm thick, is investigated as a support for the reversed-phase descending chromatographic determination of <1 μg of 26 steroids; 14 possible solvent systems are suggested. The steroids are eluted with benzene in 2-ml portions, and evaporated to dryness at 50° under N. Readings are taken in a spectrofluorimeter 2 hr. after addition of 30N-H_2SO_4 (2 ml); 58% recoveries of cortisol, and constant recoveries of corticosterone and aldosterone from amounts <1 μg are reported.

M. A. Ellis

4797. **Separation of steroid oestrogens by means of a chromatographic plate.** M. Barbier and S. I. Zav'yalov. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1960, (7), 1309–1310; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (9), Abstr. No. 9S63.—A method is given for the chromatographic separation of oestrogens on a glass plate coated with a mixture of silicic acid (5%) and gypsum (or starch) (95%) in 3 times its vol. of water. The plate is set aside for 30 min. in a horizontal position and is then activated by heating at 110° for 1 hr. Chromatography is carried out with pentane - ethyl acetate (3:2 or 9:1) by the ascending technique. By this method the following were separated—oestrone, oestrone acetate, oestrone 3-methyl ether, oestradiol, 17-ethynyloestradiol 3-methyl ether and equilin. Mixtures of oestrone and luminoestrone and of equilin and isoequilenin are not separated. The spots are located by exposure to iodine vapour or by immersion in 0·5% $KMnO_4$ soln. followed by rinsing in water. With gypsum plates the chromatograms are treated with $SbCl_3$.

A. Burwood-Smith

4798. **Colorimetric and chromatographic determination of urinary oestrogens.** V. Marescotti, M. Luisi and C. Savi (Ist. di Patol. Spec. Med., Univ. Pisa, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1961, **37** (8), 363–366.—The urine is hydrolysed with acid and extracted with ether and the extract is evaporated to dryness after being washed with $NaHCO_3$ and Na_2CO_3. The residue is dissolved in ether plus CCl_4 and phenolic compounds are extracted with KOH; the extract is neutralised with H_2SO_4 and re-extracted with ether. The extract is evaporated to dryness and the residue is dissolved in ethanol - benzene (1:1) (10 ml). Total oestrogens are determined on 1 ml with quinol - H_2SO_4 followed by extraction with *p*-nitrophenol in $CHCl_3$ and measuring the extinctions at 500, 538 and 577 mμ against an oestrone standard. The dry residue from the remaining 9 ml of ethanol - benzene soln. is dissolved in the minimum amount of the same solvent and chromatographed on Whatman No. 1 paper together with standards of pure oestrone, oestradiol and oestriol. The separated spots are extracted with $CHCl_3$ and the dried residues, after removal of $CHCl_3$, are examined colorimetrically as described above. Recoveries of 4 μg of pure oestrogens added to normal urine were 89 to 96% for oestrone, 75 to 85% for oestradiol, and 85 to 97% for oestriol. The method is recommended for clinical use.

J. I. M. Jones

4799. **Estimation of urinary metabolites of administered [16-^{14}C]17β-oestradiol.** L. L. Engel, C. B. Cameron, A. Stoffyn, J. A. Alexander, O. Klein and N. D. Trofimow (Massachusetts General Hospital, Boston, U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 114–125.—The procedure comprises four steps. (*i*) The radioactivity of the urine is measured by counting in the Geiger region, either on the evaporated residue in a windowless gas-flow counter, or on similar residues incorporating [1-^{14}C]leucine as internal standard. (*ii*) Steroid conjugates are hydrolysed by a 48-hr. incubation with *Esch. coli* β-glucuronidase, then extracted with ethyl acetate satd. with H_2O, washed with $NaHCO_3$ soln. and H_2O, evaporated to dryness, and counted in 95% ethanol. (*iii*) Phenolic fractions in methanol are purified on a Dowex-2 column by elution with 5N-acetic acid in methanol, and evaporation to dryness under reduced pressure. (*iv*) 2-Methoxyoestrone, oestrone, 17β-oestradiol, 16-epi-oestriol and oestriol are separated by partition chromatography from methanolic soln. on Hyflo-Supercel, the mobile phases being (*a*) trimethylpentane (40 fractions, each of 1 column-vol.), (*b*) 1,2-dichloroethane - 2,2,4-trimethylpentane (1:1) (80 fractions, each of 1 column-vol.), and (*c*) 95% ethanol (30 ml). The evaporated residues are dissolved in 95% ethanol for counting.

M. A. Ellis

4800. **Separation of urinary 17-oxosteroids by gas chromatography.** E. O. A. Haahti, W. J. A. Vanden Heuvel and E. C. Horning (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Anal. Biochem.*, 1961, **2** (2), 182–187.—For the quant. determination of androsterone, 5β-androsterone (3α-hydroxy-5β-androstan-17-one) and dehydroepiandrosterone, two columns are required. The sample is passed through a 12-ft. column of SE-30 silicone polymer (1·5%) on Gas-Chrom P at 216° and 20 p.s.i. A second sample is passed through a 6-ft. column of neopentyl glycol succinate (0·75%) on Gas-Chrom P at 209° and 24 p.s.i. The composition is calculated from peak-area measurements, and recoveries are >95%. Chromatographic curves are given and retention times, relative to cholestane, are tabulated.

M. A. Ellis

4801. **Extension of the Porter - Silber reaction to 17-deoxy-α-ketolic steroids.** M. L. Lewbart and V. R. Mattox (Mayo Clinic, Rochester, Minn., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 559–561.—The method is based on the oxidation of 17-deoxy-α-ketolic steroids (pregnane derivatives) (4 to 60 μg) with cupric acetate to the corresponding glyoxals, followed by treatment with the Porter - Silber reagent. Beer's law was obeyed for all the steroids tested.

G. P. Cook

4802. **Chromatographic separation of enzymes for analytical purposes.** R. W. McGilvery (Dept. Biochem. Univ. Virginia Med. School, Charlottesville, U.S.A.). *Anal. Biochem.*, 1960, **1** (2), 141–150.—A sample of the soluble proteins from a tissue homogenate is passed through a column of diethylaminoethylcellulose charged with the magnesium salt of EDTA, and the percolate from this column is then passed through a column of carboxymethylcellulose, charged with the ammonium salt. The adsorbed enzymes are eluted from each column by gradient elution, with a soln. of the diammonium magnesium salt of EDTA (prep. given). To achieve rapid fractionation of the enzymes, the ratio of column length to column diameter is small, and the columns are loosely but carefully packed. Illustrative results are given for 5 commonly measured enzymes *viz*, aldolase, 6-phosphogluconic dehydrogenase, fructose diphosphatase, glucose 6-phosphate dehydrogenase and lactic dehydrogenase, and it is shown that these retain their

stability sufficiently for the determined values to represent the values for the original tissue.
D. B. PALMER

4803. Spectrophotometric method for the assay of bacterial mucopolysaccharases. H. I. Nakada, J. B. Wolfe, L. I. Hochstein and A. J. Andreoli (Scripps Clinic and Res. Foundn., La Jolla, Calif., U.S.A.). *Anal. Biochem.*, 1960, **1** (2), 168–177.—Rapid and convenient assays are described for the bacterial enzymes that catalyse the degradation of chondroitin sulphate and hyaluronate. Bacterial chondroitinase is determined by two methods. (*i*) *At pH* 7·9—The substrate is potassium chondroitin sulphate (**I**), and the extinction coeff. of the reaction mixture is determined at 1-min. intervals, over several minutes, at 232 mμ. (*ii*) *Acid method*—The substrate is **I** at pH 7·9, and aliquots of the reaction mixture are taken at set time intervals and are placed in a KCl - HCl buffer (pH 1·8) or in an ethanol - HCl mixture (≃0·1N). Any protein ppt. is removed by centrifuging and the extinction coeff. of the resulting soln. are determined at 232 mμ. This method is useful for large-scale experiments, enzymatic degradations at high substrate levels, or crude or whole-cell preparations. Bacterial hyaluronidase is determined by using a substrate of hyaluronic acid, the method being the same as for chondroitinase. Dilute enzyme soln. require stabilisation with 0·5% gum acacia soln. By modifying the pH and concn. of the soln. used, these methods can be adapted for the assay of unsaturated disaccharide-producing mucopolysaccharases. D. B. PALMER

4804. Automated assay of activities of enzymes involving the DPN⇌reduced DPN reaction. M. K. Schwartz, G. Kessler and O. Bodansky (Div. of Enzymol., Sloan-Kettering Inst. for Cancer Res., New York, U.S.A.). *J. Biol. Chem.*, 1961, **236** (4), 1207–1211.—A continuous-flow instrumental system of analysis, in which the Autoanalyzer (Skeggs, *Amer. J. Clin. Path.*, 1957, **28**, 311; Schwartz *et al.*, *Ann. N.Y. Acad. Sci.*, 1960, **87**, 616) is used, is applied to the determination of enzyme activities that depend on the reversible conversion of diphosphopyridine nucleotide into the reduced form. The method is used for the assay of lactic acid dehydrogenase, alcohol dehydrogenase, and glutamic - oxalacetic transaminase. The results agree with those obtained by manual methods.
J. N. ASHLEY

4805. Determination of ribonuclease activity. W. Fiers (State Agric. High School, Ghent, Belgium). *Anal. Biochem.*, 1961, **2** (2), 126–139.—The method is based on the depolymerisation of ribonucleic acid and precipitation of high-mol.-wt. polynucleotides. The low-mol.-wt. degradation products also resulting are determined spectrophotometrically. *Procedure*—To 2% Na ribonucleate soln. (1·5 ml) add 0·4M-buffer soln. (1·5 ml) and H_2O (1·5 ml). To 300-μl aliquots add enzyme test soln. (100 μl) and incubate. To stop the reaction, add 2 ml of a mixture of 80% aq. $Ba(ClO_4)_2$ soln. and 2-ethoxyethanol (1:9), with shaking. Set aside for 50 to 70 min., centrifuge at 1200 r.p.m. for 8 min., and measure the extinction of the supernatant liquid at 260 mμ against a non-incubated blank. Compare with a standard curve. The Beer - Lambert law is obeyed. Protein in concn. >0·05% interferes, but compensation for certain ions may be made by a correction factor. M. A. ELLIS

4806. Glutamic - oxalacetic transaminase. Determinations in barley and malt. H. Guthenberg. *Svensk BryggTidskr.*, 1961, 5–15.—*Procedure*—The ground sample (50 g) is de-fatted by extraction with ethyl ether (2 × 150 ml) for 45 min. at 4° and centrifuging. The residual meal is dried *in vacuo* and extracted at 4° in a high-speed blender with 150 ml of 0·02M-sodium phosphate (pH 8·0) of which 75 ml is in the frozen state. The mixture is transferred to a centrifuge tube with the phosphate soln. (100 ml) and centrifuged at 2000 r.p.m. The supernatant liquid is collected, and two further extracts are made, each with 250 ml of phosphate soln. The extracts are combined, and 1 ml is dialysed against 2 litres of the phosphate soln. at 4°. To a spectrophotometer cell are added, at 25°, reagent *A* [pH 8·0, containing aspartic acid, reduced diphosphopyridine nucleotide, tri(hydroxymethyl)-methylamine buffer and EDTA] (3 ml), the sample extract (20 or 40 μl) and pyridoxal phosphate soln. (40 μg per ml) (20 or 40 μl). Reagent *B* [containing α-oxoglutaric acid and tri(hydroxymethyl)methylamine buffer] (1 ml) is added and the decrease in extinction is measured at 340 mμ and 25° against water. Transaminase activity is expressed as (Karmen units × 10) per min. per g of dry sample. (*Cf.* Karmen, *J. Clin. Invest.*, 1955, **34**, 131.)
R. E. E.

4807. Warburg's optical test. E. H. M. Greuell (Res. Lab. Kon. Ned. Gist- en Spiritusfabr. N.V., Delft, Netherlands). *Chem. Weekbl.*, 1961, **57** (6), 65–74.—A review, with 206 references, is given of the nature and scope of Warburg's optical test, which is an enzymatic method that can be used to determine a great number of organic compounds and enzymes. The method is based on the measurement of the change in extinction at 340 mμ that accompanies the transition of pyridine nucleotides into reduced pyridine nucleotides and vice versa. A number of factors that are important in this method are discussed. Many applications are listed. M. J. MAURICE

See also Abstracts—**4543**, Liquid scintillation counting of ^{14}C. **4544**, Determination of ^{14}C on chromatograms. **4695**, Analysis of oligosaccharides. **4815**, Colorimetric assay for diosgenin. **4820**, Determination of barbiturates. **4825**, Fatty acids in suppository bases. **4830**, Polarimetric determination of starch. **4892**, Starch electrophoresis of haemoglobin. **4893**, Resolution of serum electrophoresis patterns.

Pharmaceutical analysis

4808. Biological standardisation and the analyst. A review. J. W. Lightbown (Dept. of Biol. Standards, Nat. Inst. for Med. Res., Mill Hill, London, N.W.7). *Analyst*, 1961, **86**, 216–230.—Direct and comparative measurements of biological activity are described, a comparison is made between non-biological and biological assay methods and the requirements for valid biological assay are considered. International co-ordination of biological standardisation and collaborative international assays are discussed, with a classification of international biological preparations and units of activity. Future developments are indicated. International standards and their reference preparations (excluding antibiotics) are listed and the potencies

of international standards for antibiotics and their reference preparations are tabulated. (38 references.) A. O. JONES

4809. **Column partition chromatography in pharmaceutical analysis.** J. A. P. Stroes (Pharm. Lab., Rijksuniv., Groningen, Netherlands). *Pharm. Weekbl.*, 1961, **96** (8), 289–299 (in English).—Mixtures of acetylsalicylic acid, phenacetin and caffeine are analysed by column partition chromatography on Celite 545, the lower half of which is treated with 4N-H_2SO_4 and the upper half with $NaHCO_3$. A soln. of the mixture in $CHCl_3$ and ethyl ether is transferred to the column. Phenacetin is eluted with ether and determined spectrophotometrically at 285 mμ after evaporation of the solvent and dissolution in $CHCl_3$, then caffeine is eluted with $CHCl_3$ and determined by an extinction measurement at 276 mμ. Acetylsalicylic acid is eluted with a soln. of acetic acid in $CHCl_3$ (1%) and determined spectrophotometrically at 280 mμ. For the separation of barbitone and aprobarbital, a soln. of the mixture in $CHCl_3$ is transferred to a column packed with Celite 545 that has been treated with buffer soln. (pH 9). Aprobarbital is eluted with $CHCl_3$, satd. with buffer soln. (pH 9), and subsequently determined by evaporation of the eluate to dryness, dissolution of the residue in ethanol and dilution with water and buffer soln. (pH 10·5), followed by an extinction measurement at 240 mμ. Barbitone is eluted with ethyl ether, satd. with buffer soln. (pH 9). After removal of the ether from the eluate and addition of water, ethanol and buffer soln. (pH 10·5), the extinction at 240 mμ is measured. M. J. MAURICE

4810. **Application of paper chromatography and electrophoresis to the assay of pharmaceutical products.** H. Schriftman and R. C. Shultz (Wyeth Lab. Inc., Radnor, Pa., U.S.A.). *J. Pharm. Sci.*, 1961, **50** (4), 332–336.—Use two-dimensional paper chromatography, with $CHCl_3$ - ethyl ether (1:1) and butanol - acetic acid - H_2O (5:1:3) as solvents, to separate phenylephrine (**I**), chlorpheniramine (**II**) and dextromethorphan (**III**). Use paper electrophoresis in acetate buffer solution (pH 4) (ionic strength 0·1) to separate **I**, **II**, **III** and *p*-acetamidophenol (**IV**), and to separate meperidine (**V**) from decomposition products and from promethazine. Use paper chromatography with butanol - acetic acid - H_2O (5:1:3) to separate ethynyloestradiol (**VI**) from decomposition products extracted from tablets or capsules with CCl_4, and to separate procaine (**VII**) from amethocaine (**VIII**). Detect **II**, **III**, **V**, **VII** and **VIII** by a modified Dragendorff spray reagent and **I**, **IV**, **VI** and **VII** by a spray reagent containing diazotised sulphanilic acid. Measure the spots by quant. photo-electric densitometry. The accuracy is comparable with that of conventional colorimetric and spectrophotometric methods. (*Cf. Anal. Abstr.*, 1957, **4**, 3096; 1959, **6**, 3171.) A. R. ROGERS

4811. **Titration of organic bases and salts in a non-aqueous medium.** H. Feltkamp (Pharm.-Chem. Inst., Univ., Tübingen, Germany). *Dtsch. ApothZtg*, 1961, **101** (8), 207–210.—Methods are described for the non-aq. titration of alkaloidal salts, which are determined in anhydrous ointments by melting in the solvent and titration *in situ*. Inorganic salts are dissolved in formic acid and added to acetic anhydride (10 vol.) before titration. Strong bases in the presence of weaker bases are titrated in $CHCl_3$ (containing acetic acid or ethyl acetate if necessary) in the presence of bromophenol blue until the soln. becomes colourless or faintly yellow. The weaker base is then determined by adding acetic anhydride and malachite green, and continuing the titration. A. G. COOPER

4812. **Use of paper chromatography for checking methods for the determination of morphine in opium. II.** J. Büchi and R. Huber (Pharm. Inst., Eidg. Tech. Hochsch., Zürich, Switzerland). *Pharm. Acta Helv.*, 1961, **36** (4), 268–279 (in German).—The methods of Eder and Wäckerlin (*cf. J. Pharm. Pharmacol.*, 1937, **10**, 680) and Mannich (*cf. Arch. Pharm.*, 1942, **280**, 386) and some modifications have been examined. (*Cf. Pharm. Acta Helv.*, 1961, **36**, 119.) A. R. ROGERS

4813. **Analysis of ergot alkaloids. IV. Separation and detection of the alkaloids of the clavine series.** M. Klavehn and H. Rochelmeyer (Pharm. Inst., Johannes Gutenberg Univ., Mainz, Germany). *Dtsch. ApothZtg*, 1961, **101** (17), 477–481.—The alkaloids of the clavine series are separated by thin-layer chromatography on silica-gel plates with either $CHCl_3$ - ethanol (10:1) or, better, $CHCl_3$ - ethanol (19:1) followed by ethyl acetate - ethanol - dimethylformamide (17:2:1) as developing solvent, and detected by u.v. fluorescence or by colour reaction with van Urk's reagent. A. R. ROGERS

4814. **Determination of some pharmaceutical products in non-aqueous medium.** P. Kerny, J.-P. Billon and F. Bigeard (Lab. de Rech. Anal., Soc. des Usines Chim., Rhône-Poulenc, Vitry-sur-Seine, France). *Ann. Pharm. Franç.*, 1960, **18** (12), 901–906.—The preparation and use of $HClO_4$ is described for the non-aqueous titration of amphetamine sulphate, phenylephrine hydrochloride, quinine sulphate, sodium benzoate, levomepromazine acid maleate, mepyramine maleate, chloroquine sulphate and pyrimethamine. The inadvisability of having an excess of acetic anhydride present in the acetic acid is discussed. (*Cf. Anal. Abstr.*, 1960, **7**, 1897.) E. J. H. BIRCH

4815. **Colorimetric assay for diosgenin and related compounds.** S. C. Slack and W. J. Mader (Ciba Pharmaceutical Products Inc., Summit, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 625–627.—Diosgenin reacts with $HClO_4$ to produce a yellow chromogen which has an absorption maximum at 410 mμ. The colour produced reaches a maximum intensity after 5 min. and is stable for a further 30 min. The assay has a coeff. of variation of 1·1% and compares reasonably well with the results obtained by a chromatographic method. G. P. COOK

4816. **Spectrochromatographic method for the determination of dirhein in rhubarb rhizome.** M. Henneberg (Inst. of Med. Plants, Poznań, Poland). *Biul. Inst. Roślin Leczniczych*, 1961, **7** (1), 1–13.—The method is based on the hydrolysis procedure of Paris and Moyse (*Anal. Abstr.*, 1959, **6**, 3163), by means of which only dirhein is extracted and determined. *Procedure*—To 100 mg of powdered sample add 5N-H_2SO_4 (5 ml) and $CHCl_3$ (10 ml) and hydrolyse by heating on a boiling-water bath for 2 hr. Filter the soln., separate the $CHCl_3$ phase, and extract the aq. phase twice more with $CHCl_3$ (5 ml), heating for 15 min. each time. Wash the combined $CHCl_3$ extracts 3 times with H_2O acidified with a few drops of 0·5% HCl and dilute with

$CHCl_3$ to 25 ml. Apply five 2-ml spots of this soln. to S. & S. No. 2043b paper (17 cm × 21 cm), and develop by the ascending technique with pentane - xylene - methanol (4:2:1) for 60 to 75 min. Locate the dirhein spots (R_F 0·19 to 0·21) in u.v. light, cut out the spots and extract the dirhein by shaking with 2 ml of methanol for 1 hr. Add 5 ml of piperidine, mix, pour off the soln. from the paper and measure the extinction at 530 mμ. As a blank use a mixture of methanol and piperidine (2:5). The result is referred to a standard curve. B. K.

4817. **Iodimetric assay of natural and synthetic penicillins, 6-aminopenicillanic acid and cephalosporin C.** J. F. Alicino (Squibb Inst. Med. Res., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 648–649.—The study shows that the relationship between the iodine consumption of these compounds is stoicheiometric, and that a chemical equivalent for the various compounds can be determined experimentally. G. P. Cook

4818. **Colorimetric determination of erythromycin.** V. B. Korchagin, S. M. Semenov and L. N. Savushkina (All-Union Sci. Res. Inst. of Antibiotics). *Antibiotiki*, 1961, **6** (4), 311–314.—Add 20 to 30 ml of methanol to 90 to 100 mg of sample in a 500-ml flask and make up to vol. with water. To 2 ml of the soln. in a 25-ml flask add 10 ml of 18N-H_2SO_4, heat in a boiling-water bath for 5 min., cool, make up to vol. with 18N-H_2SO_4, and measure the extinction in a 3-cm cell with a blue filter. Find the content of erythromycin (**I**) from a calibration curve. To determine **I** in a culture liquid, filter the liquid, and dilute the filtrate with buffer soln. of pH 9·6 (5 g of $NaHCO_3$ and 4·3 g of Na_2CO_3 per litre of water) to a concn. of **I** of 80 to 250 μg per ml. To 20 ml of soln. in a 50-ml stoppered flask add 20 ml of amyl acetate (first washed with one-tenth of its vol. of 5% $NaHCO_3$ soln.), shake for 1 to 2 min. and allow the layers to separate. Shake 10 ml of the clear upper layer in a similar flask with 10 ml of 0·1N-HCl for 1 to 2 min., allow the layers to separate, take 2 ml of the clear lower layer into a 25-ml flask and continue as described above. The results on fully active material agree with those of the biological method to within ±5%, but the colorimetric method determines both active **I** and its inactivation products.

C. D. Kopkin

4819. **The microbiological assay of bacitracin and neomycin on plates with paper discs.** L. Rossi (Farm. Schiapparelli, Torino, Italy). *Farmaco, Ed. Prat.*, 1961, **16** (4), 201–206.—Assays are performed by a variant of the cylinder-plate method in which the cylinders are replaced by discs of filter-paper steeped in standard and test solutions of the antibiotics. After appropriate incubation the zones of inhibition of growth are measured. The test organisms are *Micrococcus flavus* ATCC 10240 for bacitracin and *Staph. aureus* ATCC 6388P for neomycin. J. I. M. Jones

4820. **The chemistry and analysis of hypnotics. II. The spectrophotometric determination of barbiturates.** K-H. Beyer (Landesanstalt f. Lebensmitt.-, Arzneimitt.- and gerichtl. Chem., Berlin-Charlottenburg). *Dtsch. ApothZtg*, 1961, **101** (14), 385–387.—Mix the urine, blood or other aq. sample (3 to 5 ml) with an equal vol. of phosphate buffer soln. (pH 7·4) and shake vigorously for 5 min. with $CHCl_3$ (50 ml). Extract an aliquot of the filtered $CHCl_3$ phase with 0·5N-NaOH (7 ml), centrifuge and measure the extinction of the aq. phase at the wavelength of max. absorption near 250 mμ. Beer's law is obeyed for concn. of <50 μg per ml. Measurements must be completed rapidly with *N*-methyl- and especially thio-barbiturates. A. R. Rogers

4821. **Paper-chromatographic method for the determination of *p*-chloroacetanilide in phenacetin.** H. Ritter, K. Mutter and J. Hofstetter (F. Hoffman-La Roche & Co. A.-G., Basle, Switzerland). *Pharm. Acta Helv.*, 1961, **36** (4), 232–237 (in German).—Apply a soln. of the sample of phenacetin (*e.g.*, 400 μg) in absolute ethanol (5 μl) to a strip of Whatman No. 1 paper, spray with 30% acetic acid soln., suspend in an atm. of H_2O vapour for 10 min. and develop by the descending technique with di-*n*-butyl ether for 2 hr. Identify *p*-chloroacetanilide (<0·2 μg) at R_F 0·7 to 0·8 by its fluorescence in u.v. light, and *p*-phenetidine (<1 μg) at R_F 0·1 to 0·2 by reaction with *p*-dimethylaminobenzaldehyde reagent. The method is semi-quant., and results for *p*-chloroacetanilide agree well with determinations based on the determination of Cl.

A. R. Rogers

4822. **Qualitative and quantitative tests for isobucaine hydrochloride.** E. G. Feldmann, J. J. Hefferren, H. M. Koehler and J. R. Reasenberg (Div. of Chem., American Dental Ass., Chicago, Ill.). *J. Pharm. Sci.*, 1961, **50** (4), 347–350.—Qualitative tests and u.v. and i.r. absorption spectra are given for isobucaine hydrochloride (**I**) which serve to identify it and to distinguish it from procaine hydrochloride and from meprylcaine hydrochloride. To assay pure **I**, titrate with $HClO_4$ in glacial acetic acid after the addition of mercuric acetate. To determine **I** in an injection soln. containing also adrenaline, either extract from alkaline soln. with 2,2,4-trimethylpentane, dilute suitably and measure the u.v. absorption at 227 mμ, or extract from alkaline soln. with $CHCl_3$ and titrate with a soln. of $HClO_4$ in dioxan. The recovery by either method is ≃99·5% with a standard deviation of ±0·7%.

A. R. Rogers

4823. **New gravimetric method for the determination of piperazine.** I. Grecu. *Farmacia, Bucharest*, 1960, **8**, 261–264.—The determination is based on the formation of a complex $[Cd(C_4H_{10}N_2)(SCN)_2]$ with an excess of Cd^{2+} in the presence of NH_4SCN. The sample is dissolved in 15 to 25 ml of H_2O, and 1 to 1·5 g of NH_4SCN (or 5 to 8 ml of 20% soln.) and 10 ml of 10% $CdSO_4$ soln. are added with continuous shaking. The ppt. is filtered off and washed with 100 ml of H_2O containing 0·2% of NH_4SCN and 0·2% of $CdSO_4$ and with a similar soln. diluted 1:3; after being washed with ethyl ether the ppt. is air-dried and weighed.

Chem. Abstr.

4824. **Properties and analysis of haloperidol and its dosage forms.** P. J. A. W. Demoen (Res. Lab. Dr. C. Janssen, Anal. Dept., Beerse, Belgium). *J. Pharm. Sci.*, 1961, **50** (4), 350–353.—To determine haloperidol [4-*p*-chlorophenyl-1-(3-*p*-fluorobenzoylpropyl)piperidin-4-ol] (**I**) in aq. soln., either evaporate to dryness, dissolve the residue in glacial acetic acid and titrate with $HClO_4$, or remove *p*-aminobenzoate ester preservatives by extraction with ethyl ether, dilute with isopropyl alcohol and measure the extinction at 244 mμ. To determine **I** in tablets, extract with warm isopropyl alcohol, filter, acidify, dilute and measure at 244 mμ.

To determine small amounts (*e.g.*, 25 μg) of **I** in urine or faeces, convert into the coloured complex with methyl orange, extract with benzene and examine the benzene layer absorptiometrically. Alternatively, separate **I** from biological material by the chromatographic method of Curry and Powell (*Nature*, 1954, **173**, 1143), burn in an atmosphere of O and determine F^- absorptiometrically (*cf.* Singer and Armstrong, *Anal. Abstr.*, 1959, **6**, 3092). A. R. ROGERS

4825. **The analysis of the fatty acids of suppository bases and emulsifying agents by paper chromatography of acylhydroxamic acids.** H. Sucker (Inst. f. angew. Chem., Univ., Erlangen, Germany). *Dtsch. ApothZtg*, 1961, **101** (16), 441–443.—The fatty acid components of the esters present in faeces, in suppository bases (such as cacao butter and Imhausen H) and in emulsifying agents (such as Tweens and Cremophors) can be separated and identified by conversion into the corresponding hydroxamic acids, chromatographic development on acetylated filter-paper with ethyl acetate - tetrahydrofuran - water (1:8:8) and production of colour with a spray of a soln. of $FeCl_3$ in a mixture of ethanol and butanol. A. R. ROGERS

See also Abstracts—**4454**, Determination of Hg. **4456**, Amperometric titration of ethacridine lactate and quinine hydrochloride. **4578**, Determination of 2-thiobarbituric acid. **4586**, Determination of As, Sb and Sn in tissues. **4683**, Analysis of alkaloids. **4695**, Analysis of oligosaccharides. **4702**, Determination of quinine. **4721**, Improved oxime method for camphor. **4759**, ^{131}I in thyroid gland. **4763**, Erythromycin in serum. **4764**, Determination of phenothiazines. **4765**, **4766**, Urine colour test for imipramine. **4767**, Urine colour test for thioridazine.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

4826. **Determination of boron in citrus fruits.** P. Dupaigne, A. Robin and H. Bogdanska. *Fruits, Paris*, 1961, **16** (2), 71–73.—Results obtained by the colorimetric method with Chromotrope 2B (C.I. Acid Red 176) for the determination of B are tabulated for different varieties of oranges treated with H_3BO_3 soln. The amounts of B in the juice and in the peel were determined, and in most cases the B had not penetrated into the juice.
J. V. RUSSO

4827. **Photometric determination of tin in food products, *e.g.*, conserves.** V. P. Sagakova and A. I. Lyubivaya. USSR Pat. 134,462 (25.12.1960). —Dry 5 g of conserve for 1 hr. at 150°, add 0·5 g of ammonium bicarbonate, and ash at 500° to a completely white residue, treating the ash with 5% H_2O_2 soln. to complete the process. Treat the ash twice with 3 ml of HCl (1:3), evaporating to dryness on the water bath, treat the residue with 15 ml of hot HCl (1:3) and filter into a 50-ml flask; wash the filter with hot water, and make the cold soln. up to vol. To 1 ml of the resulting soln. add a piece of litmus paper and titrate with 0·1N-NaOH to determine the HCl present. Then, to a tube containing sufficient N-HCl to give a total acidity, after the addition of 1 ml of test soln., of 1 milliequiv., add 2·5 ml of 20% NaCl soln. and water to 8 ml. Mix, add 1 ml of test soln. and 2 drops of fresh satd. ascorbic acid soln., again mix, add 0·5 ml of 1% gelatin soln., 0·5 ml of 0·1% ethanolic catechol violet soln. and 1 ml of M-Na acetate, mix, and after 5 min. measure the extinction at 619 mμ in a 10-mm cell against a blank. The colour with excess of reagent is green in the presence of Sn and yellow in its absence. Find the tin content from a calibration curve.
C. D. KOPKIN

4828. **Micro-method for the determination of sucrose in sugar cane.** J. W. Brough. Ann. Rep. Central Agric. Res. Station for Caroni Ltd. and Ste. Madeleine Sugar Co. Ltd., 1959–60, pp. 153–154.—A sample of juice is clarified by adding 2 g of Pb sub-acetate per 100 ml, and a 1-ml aliquot of the filtrate is diluted to 250 ml. Replicate 0·2 ml aliquots of this dilution are placed in test-tubes, and 0·8 ml of 0·025N-NaOH containing 15 mg of $NaBH_4$ is added to reduce invert sugar to mannitol. The mixture is incubated at room temperature for 1 hr. and then placed in a boiling-water bath for 5 min. Then 3 ml of 30% HCl is added cautiously, followed by 1 ml of 0·1% resorcinol soln. in 95% ethanol, with mixing. The tubes are placed in a water bath at 80° for 8 min. to develop the colour, which is read from the cooled soln. in a spectrophotometer at 490 mμ. A soln. containing 100 μg of sucrose in 0·2 ml is used as a standard. The results of five replicates are shown.
SUGAR IND. ABSTR.

4829. **Investigation of invert sugar in honey. I. Critical study of Fiehe's and Feder's reactions.** J.-A. Gautier, J. Renault and M. Julia-Alvarez (Org. Chem. Lab., Fac. of Pharm., Paris). *Ann. Falsif.*, 1961, **54**, 177–193.—Twenty-five samples of honey of varying age and source were used both before and after heating, and the effect of adding a special sample of invert sugar containing 0·65% of 5-hydroxymethylfurfuraldehyde was studied. With substantially the A.O.A.C. modification of Fiehe's reaction and a series of colour standards, the addition of between 2% and 5% of the special invert sugar could be detected. With the A.O.A.C. modification of Feder's reaction, the addition of 10% could be detected. It was impossible by either method to distinguish between heated and unheated honey. Feder's method had the advantage of being more rapid than Fiehe's method.
R. CLARKE

4830. **Criticism of the principles of the polarimetric starch determination according to Ewers.** M. Ulmann and M. Richter. *Stärke*, 1961, **13** (3), 67–75.—When determining starch by the Ewers method, two degradation phases must be distinguished. In the first phase, the starch begins to gelatinise and its specific rotation value remains unchanged. The duration of this phase depends upon the gelatinisation properties of the starch, the heat capacity of the water bath and the acid concn. In the second phase, chemical degradation takes place; the specific rotation decreases linearly with the heating time and is dependent on the reaction temperature and the acid concn. On standardising the Ewers method, certain reaction conditions (*e.g.*, heat capacity of the water bath, acid concn., reaction temperature and reaction time) can be specified accurately, but the gelatinisation characteristics of the starch vary from case to case and, consequently, the duration of the first phase and the specific rotation after a reaction time of 15 min.

will vary for different starches and even within one starch type. This polarimetric method cannot therefore be used as a general method.

SHIRLEY INST. ABSTR.

4831. **Simple test for the degree of putrefaction of raw fish.** W. Deckert (Inst. for Hygiene, Hamburg, Germany). *ChemikerZtg*, 1961, **85** (7), 221–225.—Since the evolution of volatile bases from putrefying fish is affected by factors other than age, the simple test is based on the determination of H_2S in air by the "H_2S test tube 0·01" (Drägerwerk, Lübeck) (*cf.* Dittmar and Strese, *Arbeitsschutz*, 1959, **8**, 173). The tube contains a heavy-metal salt on a colourless granular carrier, and the passage of air containing H_2S produces a brown coloration, the length of the coloured zone being proportional to the amount of H_2S passed. The test is compared with an earlier one (Deckert, *Arch. Fischereiwissenschaft*, 1960, **11**, 187) in which both H_2S and thiols were determined. The H_2S content of the air varies with the species of fish: a permissible upper limit of 20 μg per 10 litres of air from a vessel containing 500 g of fish is proposed for herrings and other fat fish, 2 μg for lean fish, and 11 μg for mixed catches.

J. P. STERN

4832. **Comparison of some methods of determining pectic substances.** L. Davignon. *Fruits, Paris*, 1960, **15** (11), 469–472.—Three methods are compared. The reference method consists in determining the Ca in the pptd. Ca pectate. Two other methods giving very similar results are (*i*) an acidimetric method with a glass electrode and (*ii*) a colorimetric method in which the extinction of the carbazole - pectic acid complex is measured at 520 to 570 mμ. J. V. RUSSO

4833. **Chlorogenic acids in coffee beans and their alteration on roasting. II. Quantitative investigations.** R. Krasemann (Kaffee-Forschungs-Lab., Heimbs u. Sohn, Braunschweig, Germany). *Arch. Pharm., Berlin*, 1961, **294** (3), 140–147.—*Procedure*—Extract raw or roasted beans (0·5 g) with 70% ethanol (5 × 10 ml) at 50° and chromatograph the extract (0·2 ml) for 18 hr. in the dark, on paper equilibrated over water for 6 hr., with butanol - acetic acid - butyl acetate - water (9:28:47:16) as solvent. Detect the individual chlorogenic acids by irradiation of the chromatogram with u.v. light, elute with 70% ethanol (10 ml) and filter through paper previously extracted with 70% ethanol. Measure the extinction of the eluates at 324 mμ against solvent used to elute chlorogenic acid-free paper strips, and determine the chlorogenic acids by reference to a standard curve. Adequate accuracy is attained with eluates containing >2 μg of acids per ml. The variation in determining chlorogenic acids in roasted coffee was ≃5%. The Slotta-Neisser procedure (*Ber. dtsch. chem. Ges.*, 1938, **71**, 1616) gives inaccurate results, since other reducing substances interfere, and recoveries of the various isomeric acids differ widely.

A. G. COOPER

4834. **Critical examination of methods of analysing hops.** M. Verzele. *Petit J. Brass.*, 1961, 119-122.—The major proportion (70 to 100%) of the bitterness of beer is due to the isohumulones formed from the α-acids of the hops during wort boiling, and the determination of these compounds provides a satisfactory measure of the bitterness. Methods of determination of the α-acids of hops (gravimetric, conductimetric, potentiometric, polarimetric and spectrophotometric) are outlined and their relative merits are briefly discussed. Owing to difficulties in obtaining a representative sample from a pocket of hops, analytical variations up to 15% are normal, so that simplicity and rapidity are the main considerations in selecting the method of analysis. The following polarimetric procedure has proved satisfactory. An aliquot (10 g) of a ground sample of hops (50 g) is placed on a column of activated charcoal (1 g) and the column is washed with ethyl ether containing SO_3 (100 ml). The percolate is made up to 100 ml and its optical rotation is measured in a 20-cm tube, and multiplied by 2·4 to give the α-acid content of the hops; 12 analyses can be completed in 3 hr. R. E. E.

4835. **Determination of oxidisable substances in beer.** J. L. Owades and F. Zientara. *Amer. Brewer*, 1961, Feb., 33–41.—The colorimetric method described is based on the reaction of oxidisable substances with a soln. of 1,1-diphenyl-2-picrylhydrazyl (**I**) (prep. described) which reacts with thiols, polyhydric phenols, aromatic diamines and enediols, but not with sugars, pyrimidines, bisulphites or, in general, amino-acids. The reaction is rapid with cysteine, ascorbates and reductones, but relatively slow with glutathione, melanoidin and tannins. The oxidisable substances in beer are classified into two groups, one reacting within 5 min. and the other more slowly. For the determination, the beer (0·2 ml) is mixed with solvent [8% of KCl in 2-methoxyethanol - water (1:1)] (8 ml) and 10^{-3}M-ethanolic **I** (0·25 ml). The vol. is immediately made up to 10 ml with solvent, and the extinctions are measured at 520 mμ against the solvent after 5, 10 and 30 min. A control (0·25 ml of **I** soln. made up to 10 ml with solvent) is also measured. The amount of oxidisable substance reacting in a given time is calculated from the difference between the readings for the control and the beer mixture. Results are quoted.

R. E. E.

4836. **Factors which influence laboratory attenuation-limit results. Determination of attenuation limit without fermentation.** H. R. Stocker. *Schweiz. BrauRdsch.*, 1961, **72**, 41–44.—Difficulties arising in laboratory determinations of the attenuation limit of wort by fermentation, which render the method unsuitable for relating the laboratory results to full-scale practice, are discussed. Three unspecified yeast strains were found to ferment maltotriose, maltose, glucose, sucrose and fructose completely, but did not attack any other wort sugar, and it is therefore proposed to measure attenuation limits by determining the individual sugars named, together with total wort carbohydrate. A suitable wort aliquot is submitted to paper chromatography or electrophoresis, and the separated spots are revealed by spraying the paper on both sides with 0·1M-$AgNO_3$ - 5N-aq. NH_3 (1:1) and measured photometrically. The extinction values are then plotted and the area integrals measured planimetrically. Sugars higher than maltotetrose give more reproducible results if, before spraying with ammoniacal $AgNO_3$, the paper is washed with ethanol, lightly sprayed with 10% H_3PO_4 soln., dried at 100° and re-washed with ethanol. Colour intensities are improved by dipping the dried strips in a soln. of 1-bromonaphthalene in liquid paraffin. Excellent agreement is obtained between results by the present method and those by the conventional method of fermentation by a massive inoculum of yeast. R. E. E.

4837. **Paper-chromatographic determination of fermentable sugars in comparison with attentuation by different yeasts.** W. Kleber, U. D. Runkel and I. Seyfarth (Wissenschaftl. Sta. f. Brauerei, München). *Brauwissenschaft*, 1961, **14** (2), 65–70.—The sugars were separated by ascending chromatography with n-butanol - pyridine - water (6:4:3) containing 0·1% of Flavognost (2-aminoethyl diphenylborinate), which increases the R_F values of aldoses. The spots were revealed by means of 2% diphenylamine in acetone - 2% aniline in acetone - 85% phosphoric acid (5:5:1). After being dried for 10 min. at 80° the chromatogram was rendered transparent with Elphor transparency fluid and the sugars were determined by direct photometry in an Elphor photometer and planimetric measurement of the areas. Good agreement was obtained between calibration curves for a mixture of glucose, fructose, sucrose and maltose and those for the individual sugars at the same concn.

J. Inst. Brewing Abstr.

4838. **Determination of ethyl acetate in wine by gas chromatography.** P. Ribéreau-Gayon (Lab. d'Oenologie et Chim. Agric., Fac. des Sci., Bordeaux). *Chim. Anal.*, 1961, **43** (4), 161–164.—*Procedure*—Distil 100 ml of the wine and collect exactly 20 ml. Inject 10 to 40 μl of the distillate into the gas stream of the chromatograph. The column (2 metres) is packed with polyoxyethylene glycol (Perkin-Elmer column, type K). The operating temp. is 95° and the carrier gas is He at an inlet pressure of 0·7 kg per sq. cm. The content of ethyl acetate is obtained by comparing the peak height with a standard curve (0 to 200 mg per litre). Results compare well with those by the chemical method.

R. A. Hendey

4839. **Bellier index of the preserving oil from sardines in olive oil.** G. Valentinis (Lab. Chim. Provinc. d'Igiene, Udine, Italy). *Riv. Ital. Sostanze Grasse*, 1961, **38** (1), 67–68.—The use of the Bellier index as a criterion of the quality of olive oil from preserved sardines is considered. From 80 samples, of Moroccan origin, the oil obtained by filtration showed the following distribution of indexes—> 18, 76·2%; 18 to 20, 11·2%; 20 to 22, 3·75%; and 22 to 33, 8·75%. On the basis of a limit of 18, the first group could be considered as genuine, the second as suspect, and the last two as adulterated.

L. A. O'Neill

4840. **Gas chromatography of free fatty acids. The analysis of saturated and unsaturated fatty acids from hexoic to arachidic.** W. Stuve (Hauptlab., Margarine-Union G.m.b.H., Hamburg-Bahrenfeld, Germany). *Fette, Seif., Anstrichmitt.*, 1961, **63** (4), 325–329.—A method is described by which saturated and unsaturated fatty acids with chain lengths from C_6 to C_{20} can be separated as easily as their methyl esters. Completely symmetrical elution bands are obtained by the use of high temp., low fatty acid concn. and a stationary phase which can form H-bridge bonds with the fatty acids. The glass column used was 138 cm long with an internal diameter of 0·4 cm. The carrier material was Celite 545 (particle size 0·15 to 0·2 mm), the stationary phase was Reoplex 400 treated with ethyl acetate and the carrier gas was Ar. Results are given and discussed.

I. Dickinson

4841. **New solvent system for separation of fatty acids, C_{10} to C_{18}, by countercurrent distribution.** F. Will, III (Aluminum Co. of America, New Kensington, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 647–648.—Fatty acids from C_{10} to C_{16} can be separated from each other by the countercurrent distribution technique with light petroleum as the upper layer and dimethyl sulphoxide - n-octanol (9:1) as the lower layer.

G. P. Cook

4842. **Quantitative analysis of mixtures of higher saturated fatty acids (C_{12} to C_{20}) after chromatographic separation on paper.** G. Ceresa (Staz. Chim.-Agr. Sper., Torino, Italy). *Ann. Sper. Agr.*, 1960, **14** (4, Suppl.), 121–140.—Higher fatty acids are determined by reversed-phase chromatography on S. & S. 2043b paper that has been immersed in a 30% benzene soln. of purified petroleum hydrocarbon (undecane) prepared from the 190° to 220° fraction of commercial petroleum by the urea-inclusion method of Zimmerschied *et al.* (*Ind. Eng. Chem.*, 1950, **42**, 1300). A line of the sample soln. in toluene is applied across the paper strip and, after equilibration with the developing solvent [prepared by saturating acetic acid (100 ml) with the purified hydrocarbon (10 ml) at the temp. of the developing tank and adding sufficient H_2O to make the concn. of actic acid 92·5%], ascending development is carried out for 24 hr. After drying the chromatogram for 30 min. at 100°, the acids are revealed by immersing the paper in Cu acetate soln. (10 ml of satd. soln. diluted to 500 ml), washing for 30 min. in running water and treating with 1% dithio-oxamide soln. The extinction of the bands is plotted against distance from the starting line in the direction of travel and the area under each of the peaks so obtained is measured. Each area (in sq. mm) is multiplied by the mol. wt. of the acid to which it refers and the ratio of this figure to the sum of the figures gives the proportion of the acid in the sample. Acids investigated, with their mean R_F values, were—lauric, 0·71; myristic, 0·58; palmitic, 0·44; stearic, 0·33; and arachidic, 0·24. The reproducibility was good and the errors were −3% for lauric and myristic, −1% for palmitic and +3% for stearic and arachidic acids.

J. I. M. Jones

4843. **Separation of glycerides of mixed fatty-acid chain-length by glass-paper chromatography.** R. L. Ory (S. Reg. Res. Lab., New Orleans, La., U.S.A.). *J. Chromatography*, 1961, **5** (2), 153–156 (in English).—Mono-olein, 1-aceto-3-olein, 1,3-diolein, 1,2-diaceto-3-olein and triolein can be separated by chromatography on glass-fibre paper impregnated with silicic acid, with 2% (v/v) of ethyl ether in 2,2,4-trimethylpentane (**I**) as solvent. Similar results are obtained with the corresponding group of stearins. The corresponding palmitins are more easily separated if 5% of ether in **I** is used. R_F values are given for these compounds, and for oleic acid, diolein adipate, stearic acid, 1-butyro-3-stearin, palmitic acid and 1-butyro-3-palmitin, with both 2% and 5% of ether in **I** as the mobile phase. As the chain length of the fatty acid increases, the R_F value increases.

R. M. Rowley

4844. **Paper chromatography of antioxidants: a simple method of identification and separation.** B. R. Roy, S. N. Mitra and P. N. Sen Gupta (Central Food Lab., Calcutta, India). *Curr. Sci.*, 1960, **29**, 132–133.—A mixture of butylated hydroxyanisole (**I**), butylated hydroxytoluene (**II**), propyl gallate (**III**) and dihydronorguaiaretic acid (**IV**) is chromatographed in a 4-hr. descending run on to a stationary phase consisting of 7% of liquid paraffin in light petroleum. The spots are revealed

with ammoniacal $AgNO_3$. **III** and **IV** give a black coloration instantly, while **I** and **II** require about 10 min. for colour development, the spot from **I** being somewhat diffused. Either methanol - H_2O (1:4) or ethyl acetate - H_2O (1:20) can be used as the mobile phase. R_F values for the antioxidants applied individually are identical with those obtained from the mixture. CHEM. ABSTR.

See also Abstracts—**4681**, **4682**, Determination of organic N. **4698**, Acraldehyde in fermentation products. **4759**, ^{131}I in vegetation and milk. **4785**, Determination of pyrithiamine in rat tissue. **4788**, Higher alcohols in fermentation products. **4806**, Glutamic - oxalacetic transaminase in barley and malt. **4825**, Analysis of fatty acids. **4863**, Organophosphorus insecticide residues. **4864**, Methyl 1-naphthylacetate in potatoes.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

4845. **Chemiluminescence determination of impurities in air or nitrogen - oxygen mixtures.** L. E. Krapivin. USSR Pat. 134,905 (10.1.1961).—The gas mixture is continuously passed under reduced pressure through a discharge tube with external electrodes between which a high-frequency glow discharge is excited, and the impurities are determined by the degree of quenching, by the impurity or its dissociation products, of the chemiluminescence due to the oxidation of NO by the atomic O formed in the discharge. The sensitivity is 1 mg of impurity per litre or, for chlorine-containing impurities, 0·05 mg per litre. The apparatus is illustrated, but no specific examples are given.
C. D. KOPKIN

4846. **Rapid micro-determination of sulphur dioxide in air by means of a detector tube.** Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Ooka-cho, Minami-ku, Yokohama). *Japan Analyst*, 1960, **9** (3), 229–232.—A blue - violet layer (diam. 2 mm, length 60 mm) of silica gel (40 to 60 mesh; residual water 20%) containing 4,4′-tetramethyldiaminodiphenylmethane (0·01% in 0·2N-H_2SO_4, 50 ml per 100 g of silica) and iodine (0·1% in 0·2% KI soln.) (50 ml) is decolorised on the passage (at 1 ml per sec.) of air containing SO_2 (1 to 300 p.p.m.), and the length of the colourless layer is almost proportional to the concn. of SO_2. By the use of two empirical diagrams for 5 to 300 and 1 to 40 p.p.m., the error is $<5\%$. K. SAITO

4847. **Micro-determination of formaldehyde in air.** A. C. Rayner and C. M. Jephcott (Ontario Dept. Health, Toronto, Canada). *Anal. Chem.*, 1961, **33** (4), 627–630.—The formaldehyde is collected by passing the air through an impinger containing 0·005N-HCl. Schiff's reagent is added to the soln. and the extinction is measured at 560 mμ; the presence of acetone increases the depth and stability of the colour. The method is sensitive to 0·1 μg of acetone per ml of collecting soln., and with a sampling period of 1 hr. a concn. as low as 5 parts per 10^9 can be determined. Some typical results for urban air are presented. G. P. COOK

4848. **Fluorescence spectra of aromatic hydrocarbons found in polluted atmosphere.** J. F. Thomas, B. D. Tebbens, E. N. Sanborn and J. M. Cripps (Univ. of Calif., Berkeley, U.S.A.). *Int. J. Air Pollut.*, 1960, **2**, 210–220.—This paper presents a method for obtaining smooth fluorescence curves directly from paper chromatograms, exemplifies the limitations inherent in the qual. and quant. aspects of fluorimetric analysis, and shows smooth fluorescence curves of hydrocarbons obtained from polluted atmospheres and compares them with those of compounds of known composition.
CHEM. ABSTR.

4849. **The detection and determination of polynuclear hydrocarbons in urban air-borne particulates. I. The benzopyrene fraction.** E. Sawicki, W. Elbert, T. W. Stanley, T. R. Hauser and F. T. Fox (Public Health Serv., Cincinnati, Ohio, U.S.A.). *Int. J. Air Pollut.*, 1960, **2**, 273–282.—A simple method for determining benzo[*a*]pyrene (**I**) in complex mixtures is described, and a comparison of the concn. of **I** in the air of 9 un-named American cities for Nov., 1958, is given. Evidence is presented for the identification of each hydrocarbon found in the benzopyrene fraction. The relative concn. of **I**, benzo[*e*]pyrene, benzo[*k*]fluoranthene, and perylene in the 9 cities is approx. constant.
CHEM. ABSTR.

4850. **Two methods for determining nitrates in water.** A. Morette and D. Halot. *Ann. Pharm. Franç.*, 1960, **18** (12), 833–845.—Determination of nitrate in water by the French official method (AFNOR T90–012) is satisfactory, though Beer's law is not obeyed, and even though a variety of nitrophenolsulphonic acids give rise to the colour. The original method of Chamot and Pratt (U.S. "Standard Methods for the Examination of Water", 9th edn., 1946), in which the nitrate affords only 6-nitrophenol-2,4-disulphonic acid, gives a systematically high result due to the method of preparing and using the standard. The modification given in U.S. "Standard Methods," 10th edn., 1955, was adopted by the World Health Organisation in 1958, and gives a better though still high result for similar reasons. A further modification is proposed in which the nitrate soln. (sample or standard) is evaporated to dryness and the residue is treated with 1 ml of the same phenol-2,4-disulphonic acid reagent as is used in the unmodified methods. After 15 min., 20 ml of H_2O is added and then 4 ml of 12N-KOH and, after mixing and setting aside for a short time, the contents are made up to 50 ml, washing in any deposited K_2SO_4, which then dissolves. The extinction is measured at 410 mμ; Beer's law is obeyed. The difficulties caused by the presence of other ions are discussed. E. J. H. BIRCH

4851. **Determination of nitrates by ultra-violet absorption.** E. Goldman and R. Jacobs (Dept. of Water & Power, Los Angeles, Calif., U.S.A.). *J. Amer. Wat. Wks Ass.*, 1961, **53** (2), 187–191.—The determination of NO_3^- in drinking water by the phenoldisulphonic acid method is considered to be inaccurate. A new method in which u.v. absorption is used gives much more consistent results, especially with acid soln. and when solid particles have been removed by filtration. To 50 ml of sample is added 1 ml of N-HCl and the extinction at 220 mμ is compared with that of distilled water. A correction for organic matter is made by measuring the extinction at 275 mμ, converting to equivalent NO_3^- at 220 mμ and subtracting from the result. B. F. FULLAN

4852. **Determination of organic nitrogen in water containing a large amount of mineral nitrogen by the micro-Kjeldahl method.** M. Ya. Dudova. *Gidrokhim. Materialy*, 1960, **30**, 164–169; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D198.—For the accurate determination of org. N in natural waters, NH_4^+, NO_3^- and NO_2^- must first be removed. Ammonium ions are removed by distillation of NH_3 after adding a borate buffer soln. (pH 7·4), and NO_3^- and NO_2^- are then reduced with $FeSO_4$ in acid medium to NO, which is removed by boiling. *Procedure*—To 100 to 500 ml of the sample in a round-bottomed flask add 10 ml of buffer soln. (54 ml of 0·1N-$Na_2B_4O_7$ plus 446 ml of 0·2M-H_3BO_3), distil off $\simeq$70% of the liquid, transfer the residue to a 100-ml Kjeldahl flask, add 1 ml of conc. H_2SO_4 and $FeSO_4.7H_2O$ (80 mg per mg of nitrate- or nitrite-N), evaporate the soln. to 3 to 5 ml, and determine org. N by the Kjeldahl method; the decomposition is carried out in the presence of $CuSO_4$, and the NH_3 is distilled off into 5 ml of 0·01N-$KH(IO_3)_2$, the excess of which is determined iodimetrically. The error is within 10%. C. D. KOPKIN

4853. **Spectrophotometric determination of submicrogram quantities of orthophosphate in natural waters.** Ken Sugawara and Satoru Kanamori (Chem. Inst., Fac. of Sci., Nagoya Univ., Chikusa-ku, Japan). *Bull. Chem. Soc. Japan*, 1961, **34** (2), 258–261 (in English).—The sensitivity of the determination of PO_4^{3-} by the solvent extraction of molybdophosphate (**I**) is increased by a single extraction of **I** with n-butanol - $CHCl_3$ (3:7) and decomposition of the **I** with NaOH. The liberated Mo is separated and determined spectrophotometrically at 475 mμ as the thiocyanate complex. As little as 0·02 to 1·00 μg of P as PO_4^{3-} can be determined in a water sample of <250 ml with an accuracy >95%. I. E. JONES

4854. **Measurement of radio-caesium, -strontium and -barium in rain-water.** G. S. McNaughton and R. N. Woodward (D.S.I.R., Div. of Nucl. Sci., Lower Hutt, New Zealand). *U.S. Atomic Energy Comm.*, Rep. NS-9, 1960. 27 pp.—The method described is suitable for the routine measurement of ^{137}Cs, ^{90}Sr and ^{140}Ba in rain-water. Carrier soln. were added to a collection tank and radionuclides in the rain-water were subsequently adsorbed at 80° on a Dowex-50 ion-exchange column. Caesium, strontium and barium fractions were obtained by successive elutions with 0·7M-HCl, 1·5M-ammonium lactate (pH 7·0) and 4M-HCl. The caesium fraction was further radiochemically purified, the carrier recovery for caesium determined by flame photometry, and the activity counted in a γ-spectrometer. The strontium and barium fractions were separately re-adsorbed on smaller resin columns, and the daughters ^{90}Y and ^{140}La were eluted, pptd., weighed as oxalates, and counted in a low-background β-counter.

NUCL. SCI. ABSTR.

4855. **A rapid method for the determination of radium in water.** P. N. Zharov. *Radiokhimiya*, 1960, **2** (5), 630–631; *Ref. Zhur., Khim.*, 1961, (10), Abstr. No. 10D69.—Radium is determined in water by preliminary co-pptn. with $CaCO_3$ in the presence of activated carbon. The sample (0·5 to 10 litres) (10^{-12} to 10^{-9} g of Ra per litre) is acidified with HCl (2 ml of conc. HCl per litre), satd. $CaCl_2$ soln. (1 ml per litre) and a little solid Na_2CO_3 to precipitate $CaCO_3$ are added, and CO_2 is removed with a stream of air; 10% Na_2CO_3 soln. (50 ml) is added, together with $\simeq$0·2 g of activated carbon to assist coagulation, the soln. is stirred and set aside for 1 to 3 hr. and the supernatant liquid is decanted off. The ppt. is filtered off and washed first with 1% Na_2CO_3 soln. and then with water. The ppt. is dissolved in HCl and re-pptd. from a smaller vol. (0·5 to 1 litre). The final ppt. is dissolved in HCl (1:3) and the filtrate ($\simeq$40 ml) is passed into a collecting vessel, which is sealed for a known time, and the accumulated Rn is measured in an electrometer. A. BURWOOD-SMITH

4856. **Determination of phenols in natural reservoirs at contents of 0·001 mg per litre or more.** V. T. Kaplin and N. G. Fesenko. *Gigiena i Sanit.*, 1960, (8), 41–43; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D220.—For each 100 ml of water add 1 ml of conc. H_2SO_4 and 1 ml of a soln. of 100 g of $CuSO_4.5H_2O$ in 1 litre (to combine with sulphides) and distil 90% of the sample to separate volatile phenols. Dilute the distillate to the original vol., and to 100 ml in a separating-funnel add 0·5 ml of buffer soln. (pH 9·8) (20 g of NH_4Cl in 100 ml of 25% aq. NH_3), 1 ml of 0·2% 4-aminophenazone soln. and 1 ml of $K_3Fe(CN)_6$ soln. (80 g per litre), and after 15 min. extract with 8 ml of $CHCl_3$ - isoamyl alcohol (1:2). Filter the lower layer and measure the extinction with a blue filter. The colour is stable for 4 to 5 hr. The minimum determinable concn. of phenols is 0·001 mg per litre; the error is within ±10%. C. D. KOPKIN

See also Abstracts—**4479**, H_2O_2 in air. **4535**, Tl in air. **4632**, Iodine in water supplies. **4718**, Analysis of polynuclear hydrocarbons. **4759**, ^{131}I in water. **4917**, Residual free Cl in water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

4857. **Colorimetric determination of sulphate in Morgan extracts of soil.** W. Y Magar and A. G. Pollard (Imperial College of Sci. and Technol., London, S.W.7). *Chem. & Ind.*, 1961, (16), 505–506.—The rapid procedure described is suitable for laboratory and field use. Air-dry soil is mixed with the Morgan reagent [Na acetate cryst. (100 g) and anhyd. acetic acid (30 ml) in 1 litre], shaken and filtered. The extract is passed through a 20-cm column of Zeo-Karb 225 (H^+ form), 50 to 60 mesh. The first 15 ml of the percolate is rejected and the next 5 ml is treated with Ba chloranilate at pH 3·0 to 3·5. The supernatant liquid after centrifuging is transferred to a suitable cell and the colour, stable for at least 15 hr., is matched against permanent colour standards in a Lovibond Comparator or measured by an absorptiometer. The recovery of up to 100 p.p.m. of SO_4^{2-} from known soln. is 96 to 105% in the range 5 to 80 p.p.m. C. B. BAINES

4858. **The determination of copper by atomic absorption spectrophotometry.** J. E. Allan (Dept. of Agric., Rukuhia Soil Res. Stn., Hamilton, New Zealand). *Spectrochim. Acta*, 1961, **17** (4), 459–466.—The determination of copper in plants, soils, soil extracts and fertilisers is described. The largest errors reported range from a recovery of 104% from a 1-g sample of chou moellier to which 3 μg of Cu was added, to a recovery of 98% from

a 2-g sample of clay soil to which 200 μg of Cu was added. Both these determinations were carried out by measurement of the intensity of the 3247·54-A line, but with the plant extract increased sensitivity was gained by adding ammonium tetramethylenedithiocarbamate and extracting into isobutyl methyl ketone before spraying into the flame. E. G. CUMMINS

4859. **Determination of the herbicides αα-dichloropropionic and αα-dichlorobutyric acids.** H. Roth (Landwirtschaftl. Versuchsst. Limburgerhof, Badische Anilin- und Sodafabrik A.-G., Ludwigshafen-am-Rhein). *Z. anal. Chem.*, 1961, **180** (5), 353–358 (in German).—The sample (≃1 g) is hydrolysed with NaOH for 2 hr. at 110° and then diluted to 200 ml. A 5-ml aliquot is treated with 2,4-dinitrophenylhydrazine and the dinitrophenylhydrazone of the α-keto-acid produced by the hydrolysis is extracted with toluene and determined photometrically. Standards must be carried through the procedure, since the yield of keto-acid is not quantitative. T. R. ANDREW

4860. **Determination of dithiocarbamates and thiuram disulphides in raw materials and formulated products.** H. Roth (Landwirtschaftl. Versuchsst. Limburgerhof, Badische Anilin- und Sodafabrik A.-G., Ludwigshafen-am-Rhein). *Angew. Chem.*, 1961, **73** (5), 167–169.—These fungicidal thio-compounds are split into CS_2 and the respective amines. The amine may be converted by 4,4′-dichlorodibenzenesulphonamide into a salt of sharp m.p. for identification. The CS_2 is determined iodimetrically after conversion into the xanthate with alcoholic alkali. The method is rapid, and accurate to within ±1%. *Procedure*—To the sample (0·2 to 0·3 g) add pyridine (3 ml) and then 85% formic acid (20 ml). Boil gently for 1 hr. while slowly passing air to entrain CS_2. Wash the CS_2 by passage through 5% Cd acetate soln. and absorb it in 2N-methanolic KOH (10 ml). Neutralise this soln. to phenolphthalein with 30% acetic acid and add 3 drops in excess. Add starch and titrate with 0·1N-methanolic iodine. J. P. STERN

4861. **Determination of pesticide residues.** H. J. Hardon (Keuringsdienst van Waren, Amsterdam, Netherlands). *Chem. Weekbl.*, 1961, **57** (8), 90–94.—Difficulties encountered in the determination of residues of pesticides, and the determination of small amounts of DDT, tetramethylthiuram disulphide, *p*-chlorobenzyl *p*-chlorophenyl sulphide and phenkapton, are discussed. M. J. MAURICE

4862. **Spot-test micro-determination of DDT and its related compounds in biological materials.** A. Irudayasamy and A. R. Natarajan (State Forensic Sci. Lab., Madras, India). *Anal. Chem.*, 1961, **33** (4), 630–632.—The DDT and its related compounds are extracted into ethanol and then nitrated. When treated with ethanolic KOH and acetone the soln. successively displays distinctive colours. As little as 1 μg of DDT can be detected. G. P. COOK

4863. **Determination of organophosphorus insecticides in vegetables. A general method for insecticide residues.** E. Q. Laws and D. J. Webley. (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London, W.C.2). *Analyst*, 1961, **86**, 249–255.—The sliced vegetable is macerated with dichloromethane. The filtered and washed extract is evaporated, the residue is dissolved in methanol, water is added and the liquid is extracted with light petroleum so that petroleum-sol. and water-sol. insecticides are separated. The light-petroleum extract, reduced in vol., is applied to a column of alumina (Brockman grade V) which is first eluted with light petroleum and then, separately, to recover Gusathion and malathion, with a mixture of light petroleum and ethyl ether. The $CHCl_3$ extract of the water-sol. fraction (also reduced in vol.) is applied to a column of active carbon which is eluted with $CHCl_3$. The organic matter in each of the three evaporated eluates is destroyed by a wet-combustion procedure with HCl, HNO_3 and $HClO_4$ after a preliminary heating under reflux with these acids. To each diluted residue aq. NH_3 is added, the excess is removed by boiling, ammonium molybdate soln. is added, the mixture is extracted with a mixture of isobutyl alcohol and benzene, the organic layer is washed with N-H_2SO_4, then shaken with $SnCl_2$ soln. and after adjustment of the vol. of the separated blue organic layer to 10 ml the extinction is measured at 730 mμ. A. O. JONES

4864. **Colorimetric determination of methyl 1-naphthylacetate in potatoes.** S. Bitny-Szlachto, M. Nikonorow and H. Przybińska-Karpińska (Military Inst. of Hyg. and Epidemiology, Warsaw, Poland). *Acta Polon. Pharm.*, 1961, **18** (1), 15–19.—The method is based on the conversion of methyl 1-napthylacetate (**I**) into naphthylacetohydroxamic acid (**II**) with hydroxylamine, oxidation of **II** with iodine, and colorimetric determination of the resulting HNO_2. *Procedure*—Extract 35 g of peelings, obtained from 100 g of potatoes, with acetone by a percolation procedure, then evaporate off the acetone and extract the residue with $CHCl_3$. Evaporate off the $CHCl_3$ on a water bath and dissolve the residue in ethanol. To an aliquot (≃3 mg of **I**) add 2 ml of 3·5M-NaOH and 2 ml of 2·5M-hydroxyammonium chloride, and after 15 min. acidify with HCl and extract (× 3) with ethyl ether. Evaporate off the ether, dissolve the residue in ethanol (1·5 ml) and apply spots (15 μl) of this soln. to Whatman No. 1 paper. Develop with benzene - acetic acid - H_2O (4:3:4) for 18 hr., then dry the chromatogram at 20°, cut out the relevant section and extract **II** with 5% Na acetate soln. (5 ml). Filter, add 0·5% sulphanilic acid in 25% acetic acid (0·5 ml) and 5 drops of iodine soln. (1·3 g in 100 ml of glacial acetic acid). After 4 min. remove the excess of iodine with 0·1N-$Na_2S_2O_3$, add 2 drops of 0·6% 1-naphthylamine in 30% acetic acid, and H_2O to 4·5 ml. After 10 min. measure the extinction in a Pulfrich photometer with a S53 filter. The result is referred to a standard curve. The recovery is >88%. B. K.

See also Abstracts—**4580**, Polarographic determination of PO_4^{3-}. **4703**, N in calcium cyanamide. **4704**, Detection of cyanamide.

5.—GENERAL TECHNIQUE AND APPARATUS

General

4865. **The use of natural gas in laboratories.** G. Méker (E.P.C.I. Société des Fours Méker, Courbevoie, France). *Chim. Anal.*, 1961, **43** (4), 191–192.—Suitable adaptations of Méker-type

burners are described for use with natural gas. Details are also given for the best conditions for heating furnaces and glass-blowing apparatus.
R. A. HENDEY

4866. **Method for drying small liquid samples.** H. G. Wager (Low Temp. Res. Sta., Downing St., Cambridge, England). *Analyst*, 1961, **86**, 266–267.—The apparatus consists of a desiccator fitted with a paddle connected by means of a vertical spindle through the lid with a motor (0·04 h.p.). The samples are placed in vessels on the floor of the desiccator together with dishes containing the desiccant (usually H_2SO_4). The vigorous agitation of the air in the desiccator by the rotating paddle effects the evaporation of 20 ml of sample in small beakers overnight. The only disadvantage is that if volatile matter (*e.g.* formic acid) is present in one sample it may contaminate the other samples.
A. O. JONES

4867. **Preparation of density-gradient columns.** C. H. Lindsley (Phys. Res. Dept., Res. Engng Div., American Enka Corp., Enka, N.C.). *J. Polym. Sci.*, 1960, **46**, 543–545.—An apparatus is described and illustrated, consisting of two 50-ml conical flasks, one inverted with respect to the other, joined by a T-tube at the top, providing a common outlet from which a delivery tube passes to the bottom of a 100-ml density-gradient cylinder, and by a T-tube at the bottom which is connected to a mercury reservoir. The flasks are filled with the appropriate liquids of different densities, and when the mercury reservoir is raised so that approx. 5 ml per min. flows into the flasks, a liquid of continuously varying density is delivered to the cylinder.
R. E. E.

4868. **Improved thermal-conductivity gas analyser for helium - carbon dioxide mixtures.** H. S. McKown (Carbide and Carbon Chemicals Co., Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. K-995, 1953, Decl. 1960. 23 pp.—In the apparatus described, three gas streams are continuously monitored with a concn. range of 18 to 70% with a precision of $\pm 0{\cdot}05\%$.
NUCL. SCI. ABSTR.

4869. **System for the determination of oxides of nitrogen.** F. Vratny (Wetherill Chem. Lab., W. Lafayette, Ind., U.S.A.). *Anal. Chim. Acta*, 1961, **24** (4), 389–390 (in English).—A description is given of an apparatus for the manometric determination of N resulting from the reaction of oxides of N with Ni at 800°. A modified Toepler pump manometer facilitates automatic pumping and circulation as well as the final measurement of the collected gases.
A. J. BENNETT

4870. **Determination of gases in metal samples by vacuum fusion. II. An apparatus for a rapid determination.** Saburo Yanagisawa and Michiharu Seki (Fac. of Engng, Keio Univ., Koganei, Tokyo). *Japan Analyst*, 1960, **9** (2), 131–135.—The earlier apparatus (*Ibid.*, 1959, **8**, 810) was improved by the use of magnetic mercury cut-offs and a rotatory McLeod gauge. The blank value was decreased to 0·003 ml (s.t.p.) per hr. at 1650° after complete de-gassing, and 0·2 g of the sample sufficed for analysis. The time taken for the determination of H, O and N was ≃20 min. and the accuracy was within ≃3%.

III. An automatic recording apparatus for micro-analysis. Saburo Yanagisawa, Michiharu Seki, Yoshikazu Hashimoto and Shigeru Nakamura. *Ibid.*, 1960, **9** (2), 135–138.—The collection and circulation of the gas was made automatic by the use of a solenoid mercury cut-off operated by the time switch of a rotating drum. For the measurement of the pressure (1 to 10^{-4} torr), a rotating McLeod gauge was operated with a small motor, and the height of the mercury column was recorded by the change in resistance of a platinum wire sealed in the gauge. Oxygen (≃0·003%) and N (≃0·004%) in nickel - chromium steel were determined by heating the sample at 1600°.
K. SAITO

4871. **A planchet-to-planchet micro-still.** M. G. Larrabee (Dept. Biophys., Johns Hopkins Univ., Baltimore, Md., U.S.A.). *Anal. Biochem.*, 1960, **1** (2), 151–157.—The use of this apparatus, which is fully described, enables small amounts of acetate or acids of comparable volatility, labelled with ^{14}C, to be separated from small volumes of soln. containing [^{14}C]-glucose and -lactate. The separation is followed by standard counting procedures. A 0·1-ml sample is used, and the distillate is received in 0·01 ml of a suitable reagent (*e.g.*, NaOH for volatile acids). The distillation takes 15 min. Advantages over other methods are that volatile materials are distilled directly from one planchet to another, thus aiding the recovery of small samples of material and simplifying the counting of the distillate and residue at each stage. Only two simple parts of the still become contaminated, and are quickly and easily washed and dried for re-use. The analysis of metabolic products of sympathetic ganglia from rats is given as an example of the use of the still.
D. B. PALMER

4872. **An improved Siwoloboff micro boiling-point method.** C. Karr, jun., and E. E. Childers (Low-Temp. Tar Lab., Bur. of Mines, U.S. Dept. of the Interior, Morgantown, W. Va.). *Anal. Chem.*, 1961, **33** (4), 655–656.—The apparatus described is designed for radiant heating, with minimum heat loss and with optimum conditions for viewing the onset of boiling. The method is applicable to high- and low-boiling compounds. Repeated determinations on new samples of the same compound were within 0·5° of the average value, which deviated less than 1° from the literature value.
C. B. BAINES

Chromatography, ion exchange, electrophoresis

4873. **Chromatographic separations.** G. Dijkstra (Unilever Res. Lab., Vlaardingen, Netherlands). *Chem. Weekbl.*, 1961, **57** (16), 189–193.—A survey is given of the various types of liquid - liquid and solid - liquid chromatography. Methods for the detection of substances in eluates are discussed, *viz*, differential refractometry, nephelometry and the occurrence of heat of adsorption on a suitable adsorbent.
M. J. MAURICE

4874. **Micro-determination of ions by means of chromatographic standards on aluminium oxide.** I. K. Tsitovich. *Izv. Vŭssh. Ucheb. Zavedenił, Khim. i. Khim. Tekhnol.*, 1960, **3** (4), 604–610; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D23.—It is shown that, for multiple-charged cations and anions, which have good sorption characteristics, there is a linear relationship between the height of the zone and the amount of ion (50 to 1000 μg) introduced to the column of alumina, the

zone height being practically unchanged in the presence of low concn. of another ion (50 to 100 μg), even if the latter is higher in the adsorption series. On this basis, a method is developed for the determination of Fe^{3+}, Cu^{2+}, AsO_4^{3-}, AsO_3^{3-}, PO_4^{3-} and other ions. The height of the alumina column is 5 cm. For the preparation of standards, through each of 15 columns (of strictly identical dimensions) is passed first 10 ml of the soln. containing 20 to 300 μg of the ion to be analysed, and then 0·5 ml of revealing agent [N-$K_4Fe(CN)_6$ for Cu^{2+} and Fe^{3+}, or N-$AgNO_3$ for PO_4^{3-}, AsO_4^{3-} and AsO_3^{3-}], the zone heights are measured, and a calibration curve is constructed. The method can be used for the analysis of agricultural materials.

C. D. KOPKIN

4875. **Simplified fraction collector for gradient elution chromatography.** A. Polson (Dept. of Pathol., Univ., Cape Town, S. Africa). *J. Chromatography*, 1961, **5** (2), 116–120 (in English).—An inexpensive and easily constructed fraction collector is described. It has been used in the chromatography of some viruses. R. M. ROWLEY

4876. **A new type of fraction collector.** C. W. van Capelleveen and J. C. de Man (Ned. Inst. Zuivelonderz., Ede, Netherlands). *Chem. Weekbl.*, 1961, **57** (5), 54–58.—Details are given of a new type of fraction collector in which 264 tubes can be arranged in the form of a spiral. The construction is simple. The distance between the end of the column and the tubes is very small. The apparatus may operate on a time basis as well as on a volume or drop-counting basis. M. J. MAURICE

4877. **A ratio-scale for the rapid determination of R_F values.** K.-H. Segel (Dtsch. Akad. Wissenschaften, Inst. für Med. und Biol., Berlin-Buch, Germany). *J. Chromatography*, 1961, **5** (2), 177–178 (in German).—A strip of elastic, 0·5 to 1 cm wide and 20 to 25 cm long, is marked with a scale of 0 to 100. The strip is laid along the middle of a 50-cm ruler, so that both scales can be seen, and one end of it is fastened so that the zeros coincide. The other end is fastened to a cursor which can be clamped in any position along the ruler. To obtain R_F values, the elastic is stretched until the length of the 0 to 100 scale equals the distance from the start of the chromatogram to the solvent front; R_F values corresponding to any intermediate distance can then be read directly.

R. M. ROWLEY

4878. **Refined direct transmission photometry of translucent sheet chromatograms. Some aspects of partition chromatography affecting interpretation of measurements.** J. W. H. Lugg and E. McEvoy-Bowe (Dept. of Biochem., Univ. W. Australia, Nedlands, Australia). *Anal. Chem.*, 1961, **33** (4), 535–541.—The assumptions and measurements involved in using direct photometry to determine the concn. of substances on paper chromatograms are theoretically investigated and studied experimentally with amino-acid - ninhydrin bands on filter-paper sheets. A suitable densitometer is described and several equations are derived.

C. B. BAINES

4879. **Rapid analysis and sample introduction in gas chromatography.** D. L. Peterson and G. W. Lundberg (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 652–653.—A simple criterion is developed by which a column packing permitting a minimum analysis time may be selected, and a sample-introduction valve is developed with which almost instantaneous sample injection is possible. In one application described, the quaternary system ethane, propane, propene and n-butane is analysed in 10 sec. on a column containing 4 in. of silica and 8 in. of alumina at 75°, with N as carrier gas.

C. B. BAINES

4880. **Double-column programmed-temperature gas chromatography.** E. M. Emery and W. E. Koerner (Org. Chem. Div., Monsanto Chemical Co., St. Louis 77, Mo., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 523–527.—By programming the temp. of a pair of symmetrical columns and passing the effluent from the second column through the reference side of the thermal-conductivity detector, compensation for the vapour-pressure increase of the column substrate is achieved and an acceptable base line at much higher temp. is obtained. A specially designed column-block is described, and two independent gas-flow controls compensate for lack of identical performance of the two columns. Automatic hold, cool and reset features are incorporated. Apiezon L and Dow-Corning silicone 710 oil have been used successfully up to 380°.

C. B. BAINES

4881. **Prediction of retention temperatures in programmed-temperature gas chromatography. A descriptive equation and computational method.** R. Rowan, jun. (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 510–515.—A practical method of calculating predicted retention temperatures is described and, with the aid of a single universally applicable chart, peak temperatures can be predicted rapidly and accurately. The method and examples of its use, and data for the construction of the chart, are given.

C. B. BAINES

4882. **New design for gas-chromatography columns.** S. A. Ryce and W. A. Bryce (Dept. of Chem., Univ. of British Columbia, Vancouver 8, B.C.). *Anal. Chem.*, 1961, **33** (4), 654.—The column design described retains the advantages with respect to uniformity of the simple U-tube and at the same time enables a long column to be contained in a comparatively small volume. The column assembly has an over-all length of 32 ft. and is only 9 in. high and 4·5 in. in diameter. C. B. BAINES

4883. **The adsorptive properties of firebrick in relation to its use as a solid support in gas - liquid chromatography.** J. Bohemen, S. H. Langer, R. H. Perrett and J. H. Purnell (Dept. Phys. Chem., Univ., Cambridge, England). *J. Chem. Soc.*, 1960, 2444–2451.—The adsorptive characteristics of Silocel firebrick is very much reduced after reaction with hexamethyldisilazane (**I**), and any remaining adsorption could be almost completely suppressed by adding trace amounts of polyoxyethylene glycol (mol. wt. 400). The possibilities of treatment of other solid supports with **I** are discussed and it is suggested that gas - solid adsorbents of any desired activity may be prepared by controlled treatment. N. E.

4884. **The ampoule technique, a simple precision method for gas-chromatographic investigations.** H. Cherdron, L. Höhr and W. Kern (Inst. f. Org. Chem., Univ., Mainz, Germany). *Angew. Chem.*, 1961, **73** (6), 215–218.—The technique is useful in the examination of the constituents and reactions

of high-boiling or solid substances, particularly polymers. The sample is sealed in an evacuated tube and submitted to the reaction (*e.g.*, pyrolysis or hydrolysis). The products are transferred, by means of the carrier gas, into the chromatography tube. The method is illustrated by the determination of components in formaldehyde - dioxolane copolymers. The method is readily adaptable to quant. determinations, utilises mild reaction conditions, permits recovery of unchanged starting material, and can be used for a variety of studies.
J. P. STERN

4885. **New technique for pyrolysing samples for gas-chromatographic analysis.** W. B. Swann and J. P. Dux (Res. and Devel. Div., American Viscose Corp., Marcus Hook, Pa.). *Anal. Chem.*, 1961, **33** (4), 654–655.—Pyrolysed samples contained in a small glass tube within a larger evacuated tube are introduced into the gas stream, where the tube is broken to release the volatile products of the pyrolysis. This technique is simpler than a distillation procedure and has the advantage over a hot-wire technique in that time and temperature for the pyrolysis are accurately controlled. It has been applied successfully to the identification of polyolefins and to copolymer analysis. C. B. BAINES

4886. **Preparation of stationary phases in gas chromatography.** Société pour la Diffusion d'Appareils de Mesure et de Contrôle. *Chim. Anal.*, 1961, **43** (4), 195–196.—Details are given for the preparation of columns for gas - solid and gas - liquid partition chromatography. For gas - solid chromatography the stationary phases discussed are silica gel, activated carbon and activated alumina, while for gas - liquid chromatography porous silicate material is coated with Carbowax, Apiezon grease or squalane. R. A. HENDEY

4887. **Use of *NN*-diformyl-2-methylpiperazine in gas chromatography.** L. C. Case (Dept. Chem. Engng, Purdue Univ., Lafayette, Ind., U.S.A.). *J. Chromatography*, 1961, **5** (2), 181–182 (in English).—*NN*-Diformyl-2-methylpiperazine distils at 200° and 5 torr without decomposition, and melts at ≃36°. It is highly polar, and can be used as a stationary phase instead of dimethylformamide or dimethylsulpholane, which are much more volatile. When used for the gas chromatography of hydrocarbons, *NN*-diformyl-2-methylpiperazine gives about the same retention times as dimethylsulpholane under the same conditions.
R. M. ROWLEY

4888. **Working methods in gas chromatography. I. Possible applications of a flame-ionisation detector.** D. Jentzsch and K. Friedrich (Bodenseewerk Perkin-Elmer & Co. G.m.b.H., Überlingen, Germany). *Z. anal. Chem.*, 1961, **180** (2), 96–109 (in German).—A flame-ionisation detector is attached to a Perkin - Elmer Fractometer, model 116E, in such a way that either it or the thermal-conductivity detector may be used at will. When the flame-ionisation detector is used in conjunction with a capillary column (0·1 to 0·2 mm diameter), no effective increase in sensitivity is observed as compared with the use of a thermal-conductivity detector and a normal column (4 to 6 mm diam.), because of the very small capacity of the capillary column. Examples are given (mainly with hydrocarbons) of the use of the flame-ionisation detector. When it is used with a normal column, and a sample vol. of 20 to 40 μl, impurities at the 10^{-9} level may be detected. When a flame-ionisation detector is used with benzene, the peak area is proportional to concn. over a very wide range. G. RUSSELL

4889. **Ion exchange.** G. J. de Jong (Ind. Mij Activit N.V., Amsterdam, Netherlands). *Chem. Weekbl.*, 1961, **57** (15), 177–181.—A short introduction is given on ion-exchange materials and some of their properties are discussed. Several types of separations that can be carried out with ion exchangers are mentioned. These methods are based on the chemical properties of the resin (exchange reactions between ions of the same type of charge, adsorption of both ions of the electrolyte and ion retardation) or on the physical properties of the ion exchanger (ion exclusion, the use of ion-exchange membranes and physical adsorption on the resin). M. J. MAURICE

4890. **Use of chlorine in cation-exchange separations.** W. J. Blaedel and E. D. Olsen (Chem. Dept., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 531–534.—During the passage of Fe^{3+} through columns of Dowex-50W resin, some reduction to Fe^{2+} occurs, impairing the efficiency of certain separations. On treating the resin with Cl, by shaking it with successive portions of aq. Cl, this reduction was prevented. The number of sulphonic acid groups in the resin decreases, and the number of weak acid groups increases. The capacity of the resin is reduced by only 1 to 3%. T. R. ANDREW

4891. **Electrophoresis.** F. P. Woodford (Lab. Phys. Chem., Rijksuniv., Leiden, Netherlands). *Chem. Weekbl.*, 1961, **57** (13), 154–159.—A survey is given of some applications of the principle of electrophoresis, namely, one- and two-dimensional zone electrophoresis, density-gradient electrophoresis, electro-decantation and forced-flow electrophoresis. M. J. MAURICE

4892. **A rapid modified starch-electrophoretic method [for haemoglobin].** J. W. McCoo and S. L. Leikin (Children's Hospital, 2125 13th St. N.W., Washington, D.C.). *Amer. J. Clin. Path.*, 1961, **35** (4), 349–352.—Purified potato starch is washed with 0·05M-barbiturate buffer (pH 8·6), made into a thick liquid paste with more buffer, and poured into a plastic mould (6 in. × 2·5 in. × 5/16 in.) with cellulose-sponge wicks (2·25 in. × 3·5 in.) inserted at each end. Excess of buffer is blotted off after allowing the paste to settle for 10 min. Three slits are made 1·5 in. from one end of the block with a 0·125 in. wide metal spatula, and about 0·05 ml of a 10% haemolysate is inserted in each slit with a 1-ml tuberculin syringe and 26-gauge needle. A triangular evaporation chamber is placed over the mould and, with the wicks dipping into buffer vessels containing 800 to 1000 ml of buffer and platinum electrodes, a current of 260 to 310 V at 20 to 30 mA is passed for 4·5 to 6 hr.
R. A. BRENAN

4893. **Analysis of electrophoresis patterns: a comparison of two methods with the aid of Rayleigh interference optics.** C. C. Curtain (Baker Med. Res. Inst., Alfred Hospital, Melbourne, Victoria). *Aust. J. Exp. Biol. Med. Sci.*, 1961, **39** (2), 197–202.—The methods of Tiselius and Kabat (*J. Exp. Med.*, 1939, **69**, 119) and Svedberg and Pedersen ("The Ultracentrifuge," Oxford Univ. Press, 1940) are studied for resolving serum electrophoresis patterns with

a photo-electric Rayleigh fringe comparator. By suitably modifying the plate-holder in the Perkin-Elmer model 38A electrophoresis instrument (details given), the first method can be successfully used. The method of Svedberg and Pedersen is less convenient, since it involves plotting the entire gradient curve. E. C. BUTTERWORTH

See also Abstracts—**4465**, Analysis of permanent gases. **4630**, Chromatography of corrosive gases. **4686**, Detection of functional groups. **4913**, Detector for gases.

Optical

4894. **Spectrographic analysis.** A. N. Zaĭdel', A. G. Zhiglinskiĭ and E. A. Karklina. USSR Pat. 136,949 (25.3.1961).—The sensitivity of spectrographic analysis is increased by the use of CO_2 to increase the pressure above atmospheric, since the diffusion of atoms from the arc discharge zone is thereby reduced. The sensitivity of the determination of Li is increased by one order by pressurising with CO_2 to 10 atmospheres; other elements for which increased sensitivity is attained by this method include Na, Al, Cu, Zn, Fe, Sn, Sb and Ni. C. D. KOPKIN

4895. **Apparatus for spectrographic analysis.** D. A. Shpatserman and A. F. Konstantinova. USSR Pat. 134,470 (25.12.1960).—Apparatus is described and illustrated for the automation of spectrographic analysis. It is claimed that 620 analyses can be carried out in 8 hr. C. D. KOPKIN

4896. **Investigation of factors influencing the accuracy of determinations by flame photometry.** S. Dobos and F. Till (L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1961, **67** (4), 183–188.—For a study of the causes of inaccuracies of measurements by flame photometry, a recording flame-spectrophotometer equipped with a modified Beckman atomiser-burner with an oxy-hydrogen turbulent flame was used. The light intensity was measured by means of a photomultiplier, and the recording apparatus was sufficiently fast to record intensity changes taking place during 0·1 to 0·2 sec. The correlation of inaccuracies with various factors, including flame height, speed of atomisation, monochromator slit-width and the time constant of the apparatus, was investigated. About one-third of the errors were attributable to frequencies >5 c/s and one-third to frequencies <0·5 c/s. The use of a time-constant of 1·65 sec. eliminated errors in the frequency range below 0·5 c/s. The graph of error *vs.* flame height passes through a minimum. B. VASZKO

4897. **Flame photometry in metallurgical problems. Utilisable working zones and quantitative sensitivity.** J. Ramírez Muñoz (Univ. Industr. de Santander, Bucaramanga, Colombia). *Inst. Hierro Acero*, 1961, **14** (74), 384–391.—The concept of a zone utilisable for flame-photometric analysis, which depends on the amount and concn. of an element, is explained, and factors restricting the zone and the effect of interferences are considered. The zones for the elements more frequently determined in metallurgy are shown in graphical form. L. A. O'NEILL

4898. **Simultaneous use of an analyser crystal for reflection and transmission in X-ray fluorescence spectrography.** E. J. Souninen (Outokumpu Oy, Helsinki, Finland). *Suomen Kem., B*, 1961, **34** (4), 45–47 (in English).—The possibility of using only one analyser crystal to measure the intensities of two different wavelengths of the same incident beam is discussed. The principle is applied to the analysis of small amounts of elements having atomic numbers from 22 to 30 in a matrix of predominantly light elements, and it appears that the method can be used with LiF and K_α lines. The second wavelength to be analysed is chosen to represent the most efficient part of the primary radiation. The method is not promising for manganese or lighter elements, for which very thin crystals would be required, but for iron and other elements with atomic numbers up to 30 it would seem possible to use crystals of standard thickness, *e.g.*, 0·5 mm. S. M. MARSH

4899. **Tables of wave numbers for the calibration of infra-red spectrometers.** I.U.P.A.C. Commission on Molecular Structure and Spectroscopy. *Pure and Appl. Chem.*, 1961, **1** (4), 699 pp.—Part I contains tables for the calibration of grating spectrometers in the range 4300 to 600 cm^{-1}. Part II gives wave numbers for the calibration of prism and small grating spectrometers (resolution 0·5 to 10 cm^{-1}) in the range 3950 to 600 cm^{-1}. N.E.

4900. **The use of plastics in the determination of the infra-red spectra of mulls and syrups.** G. J. Lawson and J. W. Purdie (Dept. of Mining and Minerals Engng, Univ., Birmingham, England). *Chem. & Ind.*, 1961, (16), 508.—Polyethylene and polytetrafluoroethylene are used as supports, as they are readily available in very thin films and because their infra-red absorptions are complementary and correspond closely to the regions masked by Nujol and Fluorolub, respectively. Spectra are easily obtained by using cheap expendable films without the care necessary when using rock-salt plates. The robust nature of the plastics allows the application of pressure in preparing samples. Plastic films can be used in the same way as polystyrene-coated plates for substances that may contaminate or undergo ionic exchange with sodium chloride or potassium bromide. Samples containing some water are readily examined without special precautions. Mulls of pure aliphatic and aromatic acids and gums and syrups have been examined, and results are as good as, or superior to, those obtained directly with rock-salt plates. C. B. BAINES

4901. **The use of organic solvents in atomic absorption spectrophotometry.** J. E. Allan (Dept. of Agric., Rukuhia Soil Res. Stn., Hamilton, New Zealand). *Spectrochim. Acta*, 1961, **17** (4), 467–473.—The addition to the aq. sample soln. of nine different solvents miscible with water has been investigated. The sensitivity obtained by the addition of acetone (20%) plus isobutyl alcohol (20%) was approx. twice that for aq. soln. Further experiments, in which the metal (copper) was complexed with ammonium tetramethylene dithiocarbamate and extracted into an organic solvent, have achieved an increase in sensitivity up to a max. of 7·3 times that which was obtained with an aq. soln. This increase was obtained with an ethyl acetate extract sprayed from an EEL 1998 atomiser. Only esters and ketones showed satisfactory behaviour in the flame. The application of other atomisers and the behaviour of other metals are included in this survey. E. G. CUMMINS

4902. **Floating comparator for colorimetric reactions in small volumes of liquid.** A. A. Pokrovskii. USSR Pat. 135,687 (15.2.1961).—A transparent plastic floating chamber for immersion in a thermostat contains a number of cylindrical nests or cells, the colorimetric or nephelometric determinations being carried out in these cells. The comparator is supported on a stand or floated in a thermostat at the required temp., screens being provided as background for viewing the soln. in the cells.

C. D. KOPKIN

4903. **Photometric determination of pH with a mixed indicator.** K. A. Seleznev and G. A. Shatalina. *Trudy Khim. i Khim. Tekhnol.* [*Gor'kii*], 1960, (2), 288–291; *Ref. Zhur., Khim.*, 1961, (6), Abstr. No. 6D38.—The method comprises the addition of an ethanolic soln. of the mixed indicator to the test soln., photometry of the resulting colour, and determination of the pH from a calibration curve. To construct the curve, mix the indicator soln. (0·04 g of methyl orange, 0·02 g of methyl red, 0·12 g of 1-naphtholphthalein and 0·08 g of phenolphthalein in 100 ml of 70% ethanol) with acetic acid - aq. NH_3 buffer soln. of increasing pH (0·4-unit intervals) in the pH range 3 to 11, measure the extinctions of the resulting soln. at 574 mμ in 1-cm cells, and construct the curve of extinction *vs.* pH, which has a descending and an ascending limb. To determine the pH of the test soln. use 5 ml of the soln. and 0·25 ml of indicator soln. If, after adding the indicator, the soln. becomes yellow or red, use the descending part of the curve; if it is blue or green, use the ascending portion. The error is $\gtrsim$0·4 pH unit.

C. D. KOPKIN

4904. **Photometric end-point determination in titrations with dyestuff indicators.** G. Scheidhauer (VEB Jenaer Glaswerk Schott & Gen., Jena, Germany). *Chem. Tech., Berlin*, 1961, **13** (2), 93–95.—The Pulfrich photometer with photoelectric attachment (Elpho) (the construction and use of which are described) is more accurate than visual methods for following titrations with dyestuff indicators and determining the end-point. A full description is given of its use in determining the difficult end-points of titrations of Ca, Mg and Zn with EDTA (**I**), with Eriochrome black T as indicator. The following improved method is described for analysing quartz sand for Ca, Mg and Zn. *Procedure*—The sand (7 to 8 g) is moistened and then heated, until fuming, with HF; conc. H_2SO_4 is added and the mixture is re-heated to remove F; 20 drops of HCl are added, the mixture is evaporated to dryness, the residue is dissolved in water and HCl, and the soln. is made up to 100 ml with water. One 50-ml portion is titrated for Ca with 0·001M-**I**, with murexide - NaCl as indicator and filter S57; a second 50-ml portion is analysed for Mg plus Ca (and hence Mg by difference) by adding aq. NH_3 - NH_4Cl buffer, filtering off pptd. hydroxides of Fe, Al and Ti, adjusting the pH to 10, adding an excess (25 ml) of 0·001M-**I** and 3 drops of 1-(2-pyridylazo)-2-naphthol indicator, and back-titrating the excess of **I** with 0·001M-$CuSO_4$ (to a yellow end-point) with filter S50 in the photometer. For Zn, a 50-ml portion of soln. (prepared and buffered and adjusted to pH 10 as in the procedure for Ca plus Mg) is titrated directly with 0·001M-**I**, with Eriochrome black T indicator and filter S57.

H. L. WHITEHEAD

4905. **Photometric analysis of elements in the presence of interfering ions by a calculation method from the [extinction] coefficient and additions [of the elements].** A. I. Shugar and Yu. A. Shugar. *Izv. Timiryazevsk. Sel.-Khoz. Akad.*, 1960, (3), 206–211; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D39.—The following method is recommended for overcoming the influence of substances that give additional colour or hinder the complete formation of the coloured compound of the component to be determined. Take V_1 ml of the soln., and then two portions each of V_2 ml such that $V_2/V_1 = n < 1$, and to the second vol. of V_2 ml add a known amount (c mg) of the component to be determined. Treat all three soln. with the necessary reagents, dilute to the same vol. and measure the extinctions. If these are respectively D_1, D_2 and D_3, then the concn. (x) of the desired component in the test soln. in mg per ml is given by the equation $x = c(D_1 - D_2)/(1 - n)(D_3 - D_2)$. Examples are given of the determination of Mg^{2+}, with Titan yellow.

C. D. KOPKIN

4906. **Increasing the sensitivity and reproducibility of the fluorescence analysis of solutions.** D. P. Shcherbov and R. N. Korzheva. Symposium: "Metodȳ Lyuminestsentnogo Analiza" Belorussk-SSR, Minsk, 1960, 43–49; *Ref. Zhur., Khim.*, 1961, (7), Abstr. No. 7D41.—Measurements are made of the intensity of fluorescence of soln. of fluorescein and Rhodamine 6G and S (C.I. Basic Red 1 and 11) excited by light from a mercury - quartz lamp (direct and with filters) and a discharge lamp (12 V, 30 W). It is shown that replacing the mercury - quartz sources in the fluorimeters by the discharge lamp with crossed filters corresponding to the spectrographic region of the fluorescing substance increases several-fold the sensitivity and reproducibility of the fluorimetric determination of many substances.

C. D. KOPKIN

4907. **Absorption-cell attachment for a Welch Densichron reflection unit.** F. J. Miller and H. C. Jones (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 651–652.—Modifications to a densitometer enable a change-over to be made from visual spot test control procedures to an instrumental method that can be used remotely within hot-cell facilities. Tests are made for NO_3^- - NO_2^- content by the brucine method, for Mn by oxidation to permanganate, and for reducing power by reaction with $Ce(SO_4)_2$ soln. Calibration curves for the various ions have the following upper limits—NO_2^-, 9 μg, and Mn, 4 μg.

C. B. BAINES

4908. **Absolute method of turbidimetric analysis.** E. J. Meehan and W. H. Beattie (Univ. of Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 632–635.—The method described, based on the measurement of turbidity at an experimentally determined wavelength at which the turbidity is proportional to the reciprocal of the wavelength, eliminates empirical comparison of known and unknown suspensions. The method can be applied to heterodisperse suspensions of spherical, non-absorbing particles of known refractive index, for which accurate Mie theory scattering coefficients are available. An example is given of application to a silver bromide sol.

C. B. BAINES

4909. **The theoretical sensitivity and linearity of photo-electric systems for polarimetry.** A. L. Rouy and B. Carroll (Chem. Dept., Rutgers, The State Univ., Newark, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 594–599.—The theoretical sensitivity and the limit of error for various photo-electric systems in

polarimetry are considered. It is shown that it is possible to develop a photo-electric scale which is linear to 1 p.p.m. and having a limit of error of about 5×10^{-6} degree. C. B. BAINES

Electrical

4910. **Automatic polarograph for use with solutions of high resistance.** P. Arthur, P. A. Lewis, N. A. Lloyd and R. K. Vanderkam (Dept. of Chem., Oklahoma State Univ., Stillwater, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 488–491.—The apparatus described is fitted with a strip-chart function plotter, the pen of which traces current while the chart measures the changing potential of the micro-electrode with respect to a reversible electrode through which no current is drawn. Polarographic curves of current *vs.* effective voltage are obtained, eliminating the iR drop. The polarograph and cell combination is well suited to studies and determinations in non-aqueous media, and the apparatus has been tested on a wide variety of organic soln. and has also been employed in titrations of water-insoluble substances in mixtures of 2,2,4-trimethylpentane with either isopropyl alcohol or n-butanol. C. B. BAINES

4911. **Apparatus for high-pressure polarography with application to polarography in liquid ammonia at 25°.** W. B. Schaap, R. F. Conley and F. C. Schmidt (Dept. of Chem., Indiana Univ., Bloomington, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 498–500.—An apparatus is described which allows polarographic studies with a dropping-mercury electrode to be carried out at elevated pressures. Polarograms obtained are normal in appearance and no experimental difficulties are encountered. Half-wave potentials measured in liquid ammonia at 25° and 10 atm. pressure are listed for Tl^{+}, Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}. The technique is useful for polarographic studies at temperatures above the normal b.p. of the solvent. C. B. BAINES

4912. **Second harmonic alternating-current polarography with a reversible electrode process.** D. E. Smith and W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 482–485.—A quantitative study of the second harmonic a.c. component which arises in a.c. polarography is presented. Results obtained agree with theoretical predictions of Tachi and Senda (*Bull. Chem. Soc. Japan*, 1955, **28**, 632). The base current present is found to be extremely low. Applications and advantages of this technique, *e.g.*, the simple electronic demands, are discussed briefly, and the circuit for the frequency selective amplifier used is given. C. B. BAINES

4913. **A vapour detector based on changes in dielectric constant.** J. D. Winefordner, D. Steinbrecher and W. E. Lear (Univ. of Florida, Gainesville, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 515–521.—A sensitive stable vapour detector is described. This consists of a variable capacitor mounted in a special cell which allows the gases to flow between its plates. The capacitor is part of a resonance circuit of an oscillator, the output of which is beat against that of a reference oscillator. Impurities produce difference frequencies which are a linear function of the amount of organic liquid introduced into the cell. Circuits for the oscillator, diode mixer and frequency meter, and a diagram of the cell, are given. Results show that the response of the detector is extremely rapid and is nearly insensitive to high carrier-gas flow-rates and variations in flow rate. The detector is less sensitive than the flame or ionisation detectors. C. B. BAINES

4914. **High-speed recording potentiometric titrator with automatic continuously-variable rate of titrant addition.** J. R. Glass and E. J. Moore (Res. Dept., Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 494–497.—A high-speed, noise-free and stable instrument is described for aqueous and non-aqueous titrations of acids in petroleum products. Instantaneous mixing and rapid response reduce the titration time to 2·5 min. The end-point overshoot is about 0·2% and reproducibility is better than 0·1%. The method is applicable to titrations in solvents of low conductivity, and is particularly useful for routine titrations of a large number of samples. A circuit diagram of the apparatus is given. C. B. BAINES

4915. **Distortion of chronopotentiograms from double-layer and surface-roughness effects.** W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1961, **33** (4), 485–487.—A discussion is given of the effects of surface roughness and double-layer capacitance on experimental chronopotentiometric potential - time curves. Methods of minimising and correcting for these effects are considered. C. B. BAINES

4916. **Chemical analysis with a convection electrode. I. A platinum wire electrode with a rotating dish as stirrer.** Tokuro Ozaki and Takao Nakayama (Fac. of Education, Shizuoka Univ., Oiwa-cho, Shizuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (1), 98–101.—A convection electrode was set up for voltammetry, by the use of a rotating dish (600 to 1200 r.p.m.) as a stirrer, which provides a stable current for electrolysis. When the current - voltage diagram is recorded between the platinum wire and a S.C.E. in 0·1M-KNO_3 containing $\simeq 10^{-5}$ M of I^{-} and in 0·1N-KCN containing Cd^{2+}, it is little affected by the rate of change in potential. The limiting current is proportional to the concn. of the ions and to the rate of current flow of the electrolyte. The sensitivity is $\simeq 10^{5}$ μA per mole per litre for both I^{-} and Cd^{2+}, at 1000 r.p.m. The effect of dissolved O is eliminated by SO_3^{2-}. K. SAITO

4917. **Correction for quenching associated with liquid scintillation counting.** G. A. Bruno and J. E. Christian (Bionucleonics Dept., Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1961, **33** (4), 650–651.—A simple accurate procedure is described for correcting counting errors due to quenching, when employing small-volume liquid-scintillation detection methods. The method is less time-consuming than existing techniques, and potential errors due to the addition of an internal standard, which may be in a different chemical form and under different solution conditions than the sample, are eliminated. C. B. BAINES

See also Abstracts—**4452**, Radiometric pptn. in filter-paper. **4543**, Liquid scintillation counting of ^{14}C. **4909**, Photo-electric systems for polarimetry.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
equivalent	equiv.
ethylenediaminetetra-acetic acid	EDTA
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_l
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

The chemical nomenclature used in the abstracts is that recommended by The Chemical Society ("Handbook for Chemical Society Authors", The Chemical Society, London, 1960), and may differ from that used in the original articles.

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